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SOLVENT EXTRACTION OF VANADIUM (IV) BY DI-2-ETHYLHEXYL
PHOSPHATE IN PRESENCE OF INORGANIC LIGANDS,
AMINE AND PYRIDINES

A Thesis

Submitted to the Faculty of Graduate Studies
In Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy

DEPARTMENT OF MINING AND METALLURGY

by

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EDMONTON, ALBERTA

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis titled "Solvent Extraction of Vanadium (IV) by Di-2-ethylhexyl Phosphate in Presence of Inorganic Ligands, Amine and Pyridines." Submitted by -

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in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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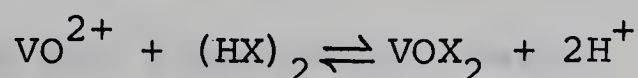
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ABSTRACT

A detailed study was made as to the solvent extraction of Vanadium (IV) by di-2-ethylhexyl phosphate. The effect of inorganic anions like chloride, nitrate and thiocyanate was to decrease the extraction in the organic phase. Tri-isooctylamine did not behave synergistically with di-2-ethylhexyl phosphate in Vanadium (IV) extraction. The substituted pyridines showed synergism in Vanadium (IV) extraction by the organophosphorous acid $(\text{HX})_2$. Extraction data combined with infrared, visible and ultraviolet spectral study showed that the Vanadium (IV) is extracted by simple chelation reaction by the organophosphorous acid.



Ultraviolet visible and electron paramagnetic resonance spectral study showed that the compound VOX_2 has the same structure as the vanadyl acetyl acetate. Infrared, visible, ultraviolet and electron paramagnetic resonance spectral study showed that the 4-substituted pyridines show synergism by the formation of 1:1 adducts of the type $\text{VOX}_2 \cdot \text{B}$. The formation constants of the adducts are determined in the different solvents.

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INTRODUCTION

For a number of years it has been recognized by the physical chemist that many substances - whether organic or inorganic, will partition between two immiscible solvents, according to the solubilities of the substances in the two solvents. The organic chemist took advantage of this phenomenon in the purification and separation of organic compounds. However, only recently has the interest in this phenomenon been applied in the field of Inorganic Chemistry and in extractive metallurgy though the extractibility of several inorganic compounds was established very early. The extractibility of the now very important inorganic compound uranyl nitrate in ether was known as early as 1842.

Though much research has been devoted to the development of more discriminating physical techniques such as spectrographic, spectrophotometric and polarographic methods with the rapid growth of chemical technology, the analytical chemist has been forced to deal with mixtures of increasing complexities. Many of these complexities arose because many elements previously considered laboratory curiosities have assumed astounding industrial significance. World War II saw the advent of nuclear energy programmes in a number of countries. Operations in atomic energy programmes requires the

elements uranium, thorium, the lanthanides and the actinides in a high state of purity. Many of the high temperature alloys now require high purity titanium, tantalum, niobium, zirconium etc. In many cases solvent extraction, or liquid-liquid extraction, has played a vital role in the separation of the desired metal or element from the undesired ones and many of the separation schemes of the analytical chemist have found plant scale operation. The classic examples are the separation of uranium from its ores, the removal of plutonium from irradiated material, and the final repurification of uranium.

Since solvent extraction permits rapid and clean separation utilising apparatus no more complicated than the separatory funnel, the radio-chemist is able to produce the carrier-free tracers of high specific activity. The examples of radio isotope separation abound in the literature; the few examples are actinium from irradiated radium , technetium from molybdenum in the separation of polonium and of beryllium. Conversely the use of radioactive isotopes has been invaluable in the investigation of solvent extraction systems, both in minimizing the analytical problems involved and in permitting studies of extremely low concentrations. For many reasons a considerable interest is now being shown in the investigation of the

extractive behavior of inorganic compounds and in the mechanism of the extraction process itself. Such studies not only extend the knowledge of the principles governing such behavior but can clearly extend the usefulness and selectivity of solvent extraction processes, both in the plant and the laboratory. Of course, the chemical knowledge of the process is by itself the most important. The extractive metallurgist utilising solvent extraction recovery processes must not only be conversant with knowledge acquired by the earlier investigators, but also investigate for the solution of the problems that arise from the plant scale operations.

In this work we shall define the word extraction as the process of extracting the metallic compounds from aqueous solutions to the water immiscible solvent phase. The metals are present in the aqueous phase as the salts of inorganic acids. The term is applied irrespective of the physico-chemical conditions under which the process is carried out or irrespective of the nature of compounds formed in the organic solvent phases. The different solvents can allow extractions by different mechanisms but the term extraction is applied universally.

Before going to represent the problems of the present work it is imperative to review in short the widely

different types of solvent extraction systems. The following chapter reviews the same. No mention will be made as to the type of apparatus that is used in industry.

CHAPTER I

EXTRACTION SYSTEMS AND THE INVESTIGATION

1. Classification of the Extraction Systems

Extraction systems are typified by diversity and complexities of the reactions that take place between the extractant (extracting solvent) and the compound to be extracted. Based on the solute-solvent interaction, or reaction, some arbitrary way to classify the extraction systems has arisen. However, in some cases there might be considerable overlapping among the different systems.

Class A - Simple Molecules

The covalent molecules like ruthenium tetroxide, iodine and the halides of Ag, Sb, As, Ce and In are known to extract as simple molecules in the organic inert solvents like hydrocarbons. Their distribution between the solvent pairs is in effect due to the relative solubilities in the two phases. This type of extraction forms one class of the extracting systems.

Class B - Complex Metal-Acid Extractions

This is much more important than the previous one because of the complexities involved in the extraction of metallic cation. The complex metal acids formed by some of the transition metals with

halides, cyanides and thiocyanides show all the properties of a strong acid. Their extraction is a bit more complex because of the appropriate number of anions necessary for the formation of the complex. These are extracted as acids, the protons of which are solvated by the solvating molecules. The solvents are usually those containing oxygen acting as the donor atom in solvation. The exact solvation number is known in many cases and the literature abounds in the examples of such extraction systems. Some representative examples are the extraction of Au (III) chloride into diethyl ether, Fe (III) chloride into diethyl ether, indium bromide by ether or of protoactinium chloride by hexane. Some compounds like molybdenum (VI) chloride, MoO_2Cl_2 exhibit this behavior, but their extraction is complicated also by the direct solvation of the cation by solvent.

Class C - Coordinately Solvated Salts

In this class of extraction systems the extraction occurs by the direct solvation of the metallic cation by the solvent. In this system the solvation number can be determined, which is the difference between the number of anionic ligands needed to make the complex neutral and the coordination number of the cation. It is also possible that a secondary solvation occurs. The oxygen containing solvents which is very important for the halometallic acid extraction is also useful

in this class; but there are very strongly basic solvents like tri-n-butyl phosphate, which are organo phosphorous compounds. There has been extensive work in this system. The most important example is the extraction of uranyl nitrate by TBP. With much more basic extractants than these compounds the behavior of the extracting agent is changed. These more basic extractants are treated in a separate class.

Class D - Liquid Cation Exchangers Solvent System

The extraction systems in which liquid cation exchangers are used form a class which has assumed tremendous importance very recently. The liquid cation exchangers are mainly acidic esters of oxyacids of phosphorous dissolved in an inert diluent. They extract metals by forming complexes with the metal cation. These complexes are insoluble in the aqueous phase. The complexes can be further solvated by additional molecules of ester. A vast amount of work has been done with extractants of this type, mostly in the case of extraction of lanthanides, actinides, and rare earths. At high acidities, the acid dissociation of the esters is reduced, and then there is a possibility that they may act as simple solvating agents. In many cases it is shown that the acidic phosphoric acid ester acts like a chelating agent to form a chelate complex. The hydrogen atom of the acidic phosphoric acid is replaced by the cation.

Class E - The Chelate Extraction System

In this class metals are complexed by acidic organic compounds to form chelate compounds with appropriate numbers of acidic organic reagents and to form neutral compounds which are generally more soluble in the organic solvents than in the aqueous phase. The solubilities of these chelate compounds in organic solvents depend upon the nature of the organic part of the chelate. If the organic part is non-polar, the complex is highly soluble in non-polar solvents, whereas any polar character of the organic part is associated with corresponding decrease in the solubility in the organic phase. The chelating agents are characterised by anions possessing two or more coordinating groups so that a stable ring structure is formed on chelation and by having a basic atom, such as nitrogen, sulfur and oxygen. The chelates usually do not need further solvation, but such solvation, if it occurs, usually increases the extraction. Examples of important bidentate anions are dithizonate, cupferrate, 8-quinolinate, acetyl acetonate, and theonyl trifluoroacetate. There are many anions of this type, some of which are found to chelate with almost any polyvalent cations under appropriate conditions.

Class F - Extraction Systems Employing Basic Reagents

In this class of extraction systems the basic reagent, usually diluted by an inert diluent, is attached to protons to form onium type compounds, like high molecular weight trialkyl ammonium salts. These compounds can extract only anionic metal complexes by ion pair formation and not by direct solvation. These extractants have been called liquid anion exchangers because of their very interesting property of exchanging anions for any other anions, specifically the anionic metal complexes. A very important example is the extraction of uranyl sulfate by triisocetylamine (TIOA) from sulfuric acid solutions to form the compound $(i-C_3NH)_4 \cdot UO_2(SO_4)_2$. High molecular weight quaternary amine salts extract by a similar mechanism, but they are effective also in non-acid solutions.

Class G - Extraction by Ion-pair Formation

In this class large cations and anions form ion pairs which do not require further solvation by a solvent. The ion pairs behave more or less like large covalent molecules, resembling Class A systems. Examples of this class are few (tetraphenyl arsonium perrhenate and cesium tetraphenyl borate).

A brief resume has been presented above to familiarise the reader with the intricate complexities and diversities in solvent extraction systems. This work

is limited to class D extraction systems. It should not be concluded that the knowledge gained in the study of other extraction systems will not be helpful in explaining the phenomena observed in the present investigation - unfortunately the truth is that there is gradual transition from one mode of behavior to another.

2. Scope of the Present Investigation

Having briefly outlined the different types of solvent extraction systems, the following discussion will deal with the specific problem of vanadium (IV) extraction.

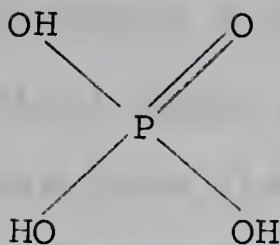
As was pointed out earlier, only recently has solvent extraction attracted the attention of the extractive metallurgists, especially the hydrometallurgists. Considerable interest has been shown in the application of solvent extraction to the hydrometallurgical processing of metals other than the rare earths and actinides. The interest in solvent extraction arose not only because it can be used as a tool for separation and purification, but also it can be used as a method of concentrating dilute metal-bearing solutions several fold.

The particular metal element with which we shall be concerned is vanadium. Vanadium is a very important alloying element in the production of cutting steels

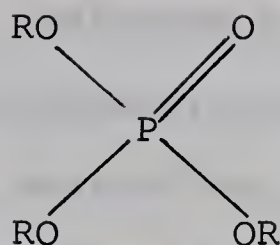
and high speed tool steels. Vanadium invariably occurs associated with many other metals.

Solvent extraction has been applied to the purification of uranium leach liquors obtained from the treatment of uranium ores by acids or bases. In the extraction of uranium from leach liquors, the vanadium is co-extracted with uranium; vanadium is then separated from uranium. The extractants which have assumed wide importance due to their chemical properties are the neutral or acidic organo phosphorous compounds. Some of these extractants have been put to commercial use in solvent extraction of rare earths because of their low volatility, fair immiscibility with water, and relative low cost.

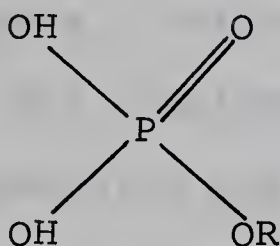
The neutral and acidic organo phosphorous compounds are organic derivatives of acids of phosphorous. The most important commercial organophosphorous compounds are the derivatives of phosphoric acid. These are prepared by the esterification of phosphoric acid. The total replacement of the hydrogen ions of the phosphoric acid by organic alkyl or aryl group produces neutral organo-phosphorous compounds. The partial replacement produces the acidic organo-phosphorous compounds. A representative structure of compounds formed is given below. R represents alkyl or aryl group.



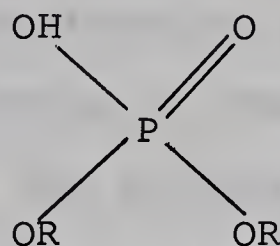
Phosphoric Acid



Trialkyl or Triaryl Phosphate



Mono-Substituted
Phosphoric Acid



Di-Substituted
Phosphoric Acid

The physical properties of the organophosphorous compounds depend, as it is expected, on the organic radical. The solubilities in water decrease and the boiling points increase with the increased number of substituent groups and with the increase in the number of carbon atoms in the R radical. The chemical properties of the extractants with respect to the selectivity and specificity towards the metal ions are liable to be influenced by the structure of the organic radical. A branching off near, or on, the carbon atom attached to oxygen atom has considerable effect in influencing the selectivity of extraction. The exact nature of this selection process is not understood very well.

The one acidic extractant which is being used extensively now for uranium extraction is Di-2-ethyl hexyl phosphate. This extractant is an alkyl derivative of

phosphoric acid with two hydroxyl hydrogens replaced by 2-ethyl hexyl radicals. Other organophosphorous extractants have also been used for the extraction of uranium from aqueous solutions. The literature is voluminous on the chemistry of extraction of uranium by these reagents. Unfortunately very little attention was paid to the chemistry of solvent extraction of other elements, especially the more common ones. The strategically important nuclear elements have taken up the major portion of the attention of workers, hence very little information can be gained from the literature as to the chemistry of vanadium extraction by organophosphorous compounds. It will be seen from the literature survey that a reasonably high extraction can only be obtained for vanadium (V) using high molecular weight alcohols, as extractants. In the treatment of leach liquors by DEHPA extractant a poor extraction of V was obtained. As the neutral organophosphorous compounds do not behave synergistically when used in conjunction with DEHPA, a new method must be sought to increase the extraction coefficient of vanadium. Unfortunately no endeavour was made in this direction because of the preoccupation with rare earth elements. The metallurgy of vanadium itself will become very important in the near future when all the easily available sources of vanadium are exhausted and substitute sources will have to be found. The now disregarded ores,

which are difficult to process, will certainly become increasingly important as new sources of vanadium.

B. Burwell rightly emphasizes this point.⁹¹ He says that very little can be gained from the literature about the chemistry and metallurgy of vanadium, and vanadium processing has developed more as an art than as a science. The metal vanadium almost always occurs as a complex ore with other elements like iron, titanium, chromium, phosphorous, lead, silica, zinc, calcium, uranium, etc. Titaniferous magnetite ore is a tremendous potential supply because it occurs in many parts of the world. The phosphate deposits of the western U.S. constitute an important source which is little used because of the problem of separation of vanadium from associated chromium, phosphorous, and iron. Solvent extraction and selective crystallization have been tried without success until now.

3. Object of Present Investigations

In view of the above problems it was felt that a start should be made to unravel the chemistry of extraction of vanadium from solutions which are complex, i.e., those which contain complex compounds. As the complexes can arise in the simplest case from the presence of simple ligands, a study should be made on how the added anions modify the extracting ability of the extractant which, in this case is Di-2-ethyl hexyl phosphoric acid, with

respect to vanadium. As the complex chemistry of vanadium is not too well known, the vanadium (IV) ion was selected for its greater stability than any other ion of vanadium. The information thus obtained for V (IV) by itself can be compared to the extraction of V (IV) from solutions containing other cations. The objective would be to study the relative degree of extraction of V (IV) in the presence of a complexing agent for a mixture of cations. The complexes of V (IV) are likely to be either less extracted or more extracted than those of other metals (Fe, Cr, Ti, etc.). Since unfortunately, the data concerning the extraction of V (IV) by DEHPA in the presence of common anions are not available, the first step would be to study the extraction behavior of V (IV) by DEHPA in the presence of added ligands in the aqueous phase. The next step naturally should be the study of the chemistry of extraction of V (IV) in the presence of a ligand by DEHPA. The same should be done for other elements before applying the DEHPA to a mixture of complexes. Since this is a long procedure, only the chemistry of vanadium extraction was selected for detailed study. Other interested workers might proceed in the same way to elucidate the mechanism of extraction for the elements Fe, Cr, Ti, etc. for the future benefit of vanadium hydrometallurgy.

In the present investigation the chemistry of

solvent extraction of V (IV) was attacked from several different angles. The main objective was to study the solvent extraction behavior of V (IV) by DEHPA in the presence of added ligands both in the aqueous and the organic phase. The work envisaged the following:

- (1) The experimental study of the dependency of the extraction of V (IV) by DEHPA on the hydrogen ion concentration.
- (2) The dependence of the extraction of vanadium (IV) by DEHPA on the concentration of Cl^- , CNS^- and NO_3^- anions in the aqueous phase. The CN^- ion was excluded because of the formation of solid complex of V in the aqueous phase.
- (3) Dependence of the extraction of V (IV) on the DEHPA concentration.
- (4) The dependence of the extraction on the concentration of V (IV) in the aqueous phase.
- (5) Possibility of the synergistic effect of the pyridine derivatives on the extraction of V (IV) by DEHPA.
- (6) UV, IR and EPR study of the adduct formation between the vanadium chelate in the organic phase and the pyridine derivatives.
- (7) Determination of the equilibrium constant and composition of the adduct formation from the spectrophotometric data.

Before proceeding to the experimental investigation of the data a brief resume of the related work of others in this field will be given.

CHAPTER II

LITERATURE SURVEY

Kuznetsove¹ studied the extraction of V (V) and V (IV) from an HCl solution of the ions into ketone. The ketones studied were methyl butyl ketone and phenyl methyl ketone. The extraction was found to increase with the increasing concentration of the hydrochloric acid. The HCl concentration range was 3-9 molar. The esters like amyl acetate were found to be good extractants. The reduction from Vanadium (V) to Vanadium (IV) was shown to be accompanied by the decrease in extraction. No mechanism study was done.

D. J. Crouse² reports that Vanadium (V) can be extracted by amines, especially the tertiary amines. The Vanadium (V) extraction was found to increase with the increase of pH, but the extraction of Vanadium (IV) was reported to be poor. No mechanism of extraction was suggested. Ogawa³ reported that 8-quinoline solution in benzene is a suitable extractant. The extraction is of analytical interest only. Blake⁴ and co-workers report that the Vanadium (IV) does not show synergistic effect in the extraction by a combination of DEHPA and a neutral organophosphorous compound. Only U (VI), Pu (IV), and Pu (VI) showed synergistic extraction with TBPO and TBP. V (IV), Al (III) and Mo showed very

little enhancement. Te (II), Ti, Th showed antisnergistic effects. H. Goto and Y. Kakita⁵ studied the extraction of Vanadium (V) and Vanadium (IV) from a strong HCl medium into the methyl isobutyl ketone. Eighty-seven percent extraction was reported for Vanadium (V) and 2.3 percent for Vanadium (IV). Milligramme quantities were used for the extractions. The process is of analytical importance only.

Santosh K. Majumder⁶ and Anil K. De reported the extraction of Vanadium (V) from 5M HCl. The extractant was tributyl phosphate. Almost quantitative extraction of V (V) can be achieved by 100 percent TBP. The effects of TBP concentration, salting out agents, and diverse ions were investigated. Vanadium (V) can be readily extracted in the presence of Cu (II), Mercury (II), Cobalt (II), Nickel (II), Barium (II), Bismuth (III), Iron (III), Chromium (III), Thorium (IV), Uranium (VI), Molybdenum (VI). There is co-extraction with copper, uranium, iron and thorium. The extracted species is $\text{VOCl}_3 \cdot 2\text{TBP}$.

Barbenko⁷ and Tolmacheve studied the extraction of Vanadium (IV) by dioxane from a solution containing 4 to 5 fold excess of nitron and a large excess of potassium thiocyanate. The extracted species was though to be a triple complex involving Vanadium, thiocyanate and dioxane. The separation has found analytical application.

Extraction of Vanadium from acid or alkaline solutions by contact with quaternary ammonium compound dissolved in a fuel oil has been reported⁹². The quaternary ammonium compounds with 1 to 4 carbon atoms and 8 to 22 carbon atoms were found effective. The process is said to be suitable for extraction from an alkaline solution. These alkaline extractants selectively extracted Vanadium from alkaline phosphate solutions, which result in a low phosphorous Vanadium product. No mention is made of the oxidation state of V or of the possible mechanism of extraction.

The separation extraction of Vanadium (IV) from basic chromium sulfate solutions has also been reported⁹³. The extractant removed only the Vanadium (IV) but not the chromium. The two types of extractants used were monophosphoric acid esters of aliphatic straight or branched chain alcohols and a mixture of the acid with tributyl phosphate, or its analogue. No mention is made of TBP showing any synergistic effect in conjunction with DEHPA or of the possible extracting mechanism.

G. Guenzler⁸ studied the extraction of Vanadium (V) from HCl solutions with TBP. The distribution coefficient was determined for 1 - 9 molar HCl as the TBP concentration in the organic phase was varied from 10 to 100%. $\text{VOCl}_3 \cdot \text{TBP}$ was the species formed in the organic phase according to the strength of the HCl. No

mention was made of Vanadium (IV).

Kuznetsove⁹ and Serya Kove studied the extraction of Vanadium (V) from solutions of vanadium and uranium in a mixture of sulphuric acid and HCl by solutions of amylacetate in toluene. The ratios of the distribution of vanadium and uranium was 100 to 10,000.

A. K. Dey and Md. Sayedur Rahman¹⁰ reported the extraction of Vanadium (V) from the aqueous solution by TTA (thenoyl trifluoro acetone) which forms a red complex with TTA in the organic phase. The studies were made with BuOH as the neutral solvent. This is supposed to be a good analytical method for pentavalent V. The noninterference of ions like Cl^- , $\text{SO}_4^{=}$, F^- , and PO_4^{3-} is noteworthy.

G. Guenzler¹¹ and P. Muehl studied the extraction of Vanadium (V) from hydrochloric acid solutions with TBP. They noticed that TBP gives higher extraction than the tri-isobutyl phosphates, but the difference is always very slight. They concluded that the coordinating capacity depends upon the P=O bond with the O acting as the donor atom to the metal ions. Other metals studied were $\text{Fe}^{(\text{III})}$, $\text{Co}^{(\text{II})}$ and $\text{Mn}^{(\text{II})}$. Pyatnitsky and R. S. Kharchenko¹² studied the extraction of metal citrate complexes in tributylamine. A host of metals was investigated. The vanadium complex was extracted to the amount of 70 to 90 percent. No mention is made about the oxidation

state of vanadium or of the possible mechanism of extraction.

D. Satyanarayana¹³ and V.P.R. Rao reported the extraction of V (V) by acetyl acetone and benzene using hydrochloric acid of 1:1 dilution and 50% acetylacetone in benzene. Extraction of 78 ± 2 percent is possible at room temperature (30°C), and the extraction is increased at lower temperature. The ions of Al (III), Bi (III), Ce (III), Cr (III), Te (III), Mo (VI), Ni (II), Th (IV), U (VI), V (IV), and Zn (II) do not interfere. Cu (II) and Mn (II) show marked adverse effects on extraction. It is reported that the V (IV) is not extracted by the reagent in the benzene phase. The extracted species in the case of benzene is supposed to be a 1:1 complex of the Vanadium (V) and the extractant.

D. Satyanarayana et al¹⁴. reported the extraction of Vanadium (V) by a mixture of acetylacetone and butyl alcohol. The foreign ions Al (III), Be (II), Sr (III), Cu (II), Fe (II), Mn (II), Ni (II), Th (IV), and V (IV) interfere very seriously. U (VI) interferes even more seriously. The above mentioned ions are coextracted. The complexing agents like EDTA, oxalate, tartrate and citrate diminished the extraction.

G. Guenzler¹⁵ studied the dependence of the distribution ratio for Vanadium (V) and Vanadium (IV) between 7 molar HCl and tri-isobutyl phosphate in benzene.

The distribution ratio for Vanadium (V) is approximately 1,000 times greater than the value for V (IV). Hence he proposed that the extraction can be used for the separation of V (V) from the tetravalent V. The Vanadium (IV) can also be effectively separated from the Fe (III).

N. I. Petunia et al¹⁶ report the extraction of Vanadium (V) from sulphuric acid solutions by higher alcohols. They found that alcohols with carbon atoms C₁₂-C₁₉ extract 100 percent of the vanadium present in the aqueous phase. An increase in the acid concentration decreases the extraction coefficient. At a sulphuric acid concentration of 5 gm/litre all the vanadium is extracted. The lowering of the extraction by the increasing acidity was attributed to the increasing oxidation potential of pentavalent vanadium and the formation of non-extractable tetravalent vanadium compound.

D. J. Crouse et al¹⁷ studied the extraction of uranium leach liquors by DEHPA. Both the uranium and vanadium were extracted by the extractant in the pH range of 1.5 - 2.0. The vanadium extraction was studied in the light of its oxidation state (penta and tetra). He found that Vanadium (IV) was extracted more than the pentavalent one. The extraction coefficient of vanadium ranged from 0.2 to 16 which is very low compared to

uranium for which values above 100 have been reported in the literature. The workers discussed the effect of sulphate and hydrogen ion concentration on the extractant. The rising concentration of sulfate ion decreases the extraction coefficient.

In the following paragraphs the studies concerning the synergistic behavior of bases used in conjunction with some acidic extracting agent will be discussed.

Dyrrsen and Henicks¹⁸ have reported the existence of synergistic action in the solvent extraction of copper (II) with solutions of dimethyl glyoxime in chloroform containing quinoline or dodecylamine. They reported the existence of an 1:1 complex obtained by graphical data, having the stability constants of $10^{2.04}$ and $10^{3.06}$ for the 1:1 adducts.

Irving and Al Niami¹⁹ also reported the existence of synergism in the extraction of Cu (II) from acetate buffers by solution of acetylacetone and quinoline or isoquinoline. They prepared the adduct in the solid state. The analysis of the solid adduct and the solvent extraction data both indicated the existence of 1:1 complex.

Irving and Al Niami¹⁹ also reported the enhanced extraction of copper by solutions of acetyl acetone in the presence of 4-methyl pyridine. The enhanced extraction is attributed to the formation of the adduct $\text{CuX}_2 \cdot \text{B}$

in the organic phase.

L. Newman²⁰ has also noticed the synergistic behavior of tri-n-octylamine in the extraction of thorium by thenoyl trifluoroacetone from HCl solutions of Th (IV). The synergistic action has been attributed to the formation of the complex $\text{Th}(\text{TTA})_4\text{R}_3\text{NHCl}$, due to the reaction $\text{Th}(\text{TTA})_4 + \text{R}_3\text{NHCl} \rightleftharpoons \text{Th}(\text{TTA})_4\text{NR}_3\text{HCl}$, where R_3NHCl represents amine hydrochloride.

D. P. Graddon and E. C. Watton²¹ studied the adduct compound formed by Cu (II)-beta-diketone chelates with pyridine derivatives. The relative stabilities of the different diketonate adducts with pyridines were compared. The infrared and visible region absorption spectra indicated a five coordinated structure for all of the prepared compounds.

W. R. May and M. M. Jones²² studied the adduct formation equilibria between bis (2,4-pentanediono) - Cu (II) and eight pyridine bases. They noticed no correlation of stability constant with the basicity of the bases. Heats of formation for these adducts showed a definite relation with the basicity of the ligands.

CHAPTER III

EXPERIMENTAL

Nomenclature

Di-2-ethylhexyl phosphoric acid, the primary extractant, is represented throughout by the symbol DEHPA. The symbol indicates - DE for di-2-ethylhexyl, P for phosphoric, A for acid. In this nomenclature it is understood that one acidic H^+ is still free and replaceable by metal ions. In this symbol no molecular complexity and diluent-extractant interactions are taken into account.

Symbols are used for other compounds as follows:

- 4EP - represents 4-ethylpyridine
- 4IPP - symbolizes 4-isopropylpyridine
- 4BP - indicates 4-Benzyl Pyridine
- 2BP - represents 2-Benzyl Pyridine
- VDEHPA - represents vanadyl di-2-ethylhexyl phosphate

Sources of Materials

Vanadium (IV) - The Vanadyl Sulfate $VOSO_4 \cdot 2H_2O$ was obtained from Fisher Scientific Company. The purity was considered adequate for the solvent extraction purpose.

DEHPA - The di-2-ethylhexyl phosphoric acid was obtained from K & K Laboratories, N.Y. The material was very viscous and colorless. The assured purity by the manufacturer was more than 95%. It was further purified by scrubbing the material with ethylene glycol to remove any monoester. Three vol. of ester was used for 1 vol. of ethylene glycol. The heavy layer of the di-ester was washed with 3 volumes of water to remove any ethylene glycol. The water was removed from the ester by long pumping at reduced pressure followed by desiccation over CaCl_2 to remove any water.

Pyridine Derivatives - The pyridine derivatives were also obtained from K & K Laboratories, N.Y. All the pyridines were redistilled at their respective boiling points and then dehydrated under vacuum over CaCl_2 . All the pyridines except beta-Collidine kept well over long periods. Beta-Collidine was redistilled before each usage. The purity test by boiling point measurement showed them to be adequate for the investigational purpose. The redistilled Pyridine derivatives showed almost exactly the boiling point indicated in the Handbook of Chemistry and Physics.

	<u>Boiling points of Pyridines (°C)</u>	
	Found	Reported
4EP	165.0	165.3
4BP	-	-
2BP	276.0	276
4IPP	178	178
beta-Collidine	196	195-6
2EP	149	148-9

All the other reagents used in this work were of reagent grade. Colorless and odorless kerosine obtained from Fisher Scientific Company was used as the diluent in extraction studies. In the spectrophotometric and E.P.R. studies different solvents were used. The solvents in these cases were benzene, hexane and chloroform.

Extraction Method & Sample Preparation

The extracting phase was the solution of DEHPA in colorless kerosine. All the extraction studies were done by using an aqueous organic volume ratio of 1:1. In the case of extraction with a mixture of a pyridine derivative and DEHPA, a standard stock solution of each was prepared in the same diluent and a predetermined aliquot of each was transferred to a 100 ml. volumetric flask. The mixture was diluted to give the desired concentration of each in the diluent. The exact concentrations of the extractants are reported in the tables.

Stock solutions of V (IV) were prepared. A 0.1 molar stock solution of vanadyl sulfate was used for the investigation of anion dependency of V(IV) extraction

by DEHPA. An aliquot of the stock solution was mixed with an aliquot of the standard solution of the anions to give the desired concentration of V (IV) and the anion. The data gives the concentrations used. The stocks for the anions were prepared when necessary by dissolving the reagent grade chemicals.

Twenty ml portions of the aqueous V (IV) solution were shaken with 20 ml portions of the organic phase. The shakings were done either in 60 ml separating funnels or in 100 ml test tubes. One hundred ml test tubes were found to be very convenient. The shakings were done mechanically by a modified Autoclave Engineers Shaker. The shaker could hold eight stoppered test tubes or four 60 ml separating funnels. The shaking was done by rapid to-and-fro motions of the shaker. Too rapid frequency of shaking was avoided to guard against emulsion formation. All the extractions were done at a constant temperature of $20 \pm 2^\circ\text{C}$.

Extraction Time - The shaking time was varied according to a preliminary experiment. In the case of extraction without pyridines or amine in the organic phase, 1 minute shaking time was found enough to reach equilibrium between the two phases. But the extraction time was increased to 5 minutes for precaution. In the case of extraction in the presence of pyridine and amine the preliminary test showed that 30 minutes time was required

for equilibrium. The time for extraction in these cases was increased to 1 hour for precaution against non-equilibrium conditions.

After shaking for the proper length of time the phases were centrifuged for about 5 minutes. The aqueous and organic phases were separated.

The distribution ratio or coefficient was obtained by the analysis of aqueous phase only. The amount that had been extracted was found by taking the difference between the initial aqueous concentration and the concentration of the aqueous phase after extraction.

Methods of Analysis

Two methods of analysis were employed - (1) Colorimetry and (2) X-Ray Fluorescence. Colorimetry - The recently developed Xylenol orange method was employed⁹⁰. The method employs the formation of a red complex with pentavalent vanadium in solution. The method was tested to find the range of its application. It was found that Beers Law was obeyed in the 5 to 50 microgram range. In this range a straight line relationship exists between the concentration and the absorbance of the measured solution.

The method could not be applied to the aqueous layer as it is applicable only to Vanadium (V) solution. In the absence of other colorimetric methods for V (IV), the Vanadium (IV) was oxidised to Vanadium (V) by suitable oxidizing agents, like ammonium persulfate in acid

solutions or nitric acid. In the nitric acid oxidation, complete removal of free nitric acid was ensured by evaporating the V (IV) solution to dryness. An aliquot of the aqueous phase was used. One ml of strong nitric acid or 0.5 gm of ammonium persulfate and 5 ml dilute HCl was added to the solution in a 50 ml beaker. The mixture was then heated to dryness. The dried-up mass was then dissolved in water and transferred to a 50 ml volumetric flask. A five ml solution of 1 percent Xylenol orange was added, followed by a 5 ml solution of ammonium-acetate-acetic acid buffer solution. The final pH of the solution should be between 3 to 5 for optimum condition for complex formation. The absorbance of the red complex was measured at 550 millimicrons against a blank of the same amount of reagents in solution. A Bausch and Lomb Spectronic 20 was found adequate for the purpose. For the standard curve the reagent grade ammonium vanadate solution was employed.

X-Ray fluorescence - This method was adopted for relatively concentrated solutions. A theoretical background of the method is given in the appendix. The method was directly applicable to the extracted aqueous layer. The method was also tried for the organic layer but in the case of organic layer the method fails because of serious interference. The cause of the interference is not known. The concentration of the metallic species in the aqueous phase was found as usual, from standard curves.

Preparation of the V (IV)-di-2-ethyl hexyl phosphate complex - For infrared, UV and E.P.R. studies the compound must be free of moisture. Special precautions were taken to ensure that the complex was moisture-free. Preparation of the complex involved shaking a 100 ml portion of 322 gm/litre benzene solution of DEHPA with five 100 ml portions of 5 gm/litre solution of V (IV). The organic phase was then centrifuged, washed with 100 ml portions of distilled water in a separation funnel. The organic phase was separated from the aqueous layer. It was then left to evaporate under vacuum in a large closed belljar connected to a vacuum pump. A green transparent wax like substance was obtained containing some benzene. The substance was freed from benzene by washing on a filter paper with three 20 ml portions of 50 percent alcohol. Some of the complex was lost through soltuion in alcohol. Finally the compound was washed with water and dried with a current of air. The product was further dehydrated to remove any moisture not chemically combined. The analyses of the product is as follows: Hypothetical molecular weight 693, observed molecular weight 1975 in benzene and 1913 in CCl_4 . Hypothetical atomic ratio V:P=1:2, found 1:1.78.

Spectrophotometric Techniques:-

The Spectrophotometric studies were carried out with three spectrophotometers. For the visible and ultra-violet region, the Perkin-Elmer 350 served the purpose.

The infrared region was investigated with the Perkin-Elmer 221 and a Perkin-Elmer 421 grating spectrophotometer. Since no special IR technique was necessary in this investigation only a few words will be said about the sampling techniques.

The visible ultraviolet sample techniques were similar to that in the IR spectra study. The spectrum between 1000 millimicrons to 350 millimicrons were obtained in parts.

Solvents for Infrared Technique - It is possible to determine the IR spectra of materials in the solid, liquid or (if it can be made gaseous without decomposition), the gaseous state. In our case the V (IV)-di-2-ethyl hexyl phosphate was found highly soluble in benzene, hexane, carbon tetrachloride and in all the pyridine derivatives studied. So it was found advantageous to employ the solution technique to the samples.

Liquid Cells

All the infrared spectra were obtained using NaCl cells. The cells were obtained in matched pairs. The cell thicknesses were 0.2 mm and 0.5 mm according to the type of solvents.

Usually before the filling of the cells special precautions were taken to clean the cells properly as foreign materials left from earlier use of the cell can also absorb. The procedure adopted was to flush the

cell with the CCl_4 after every use. Carbon tetrachloride was also found to dissolve away the pyridine derivatives. After proper flushing the cell was dried in a current of dry air, the air being forced through the cell.

Filling Cells

A syringe of a few millimeters capacity was used to fill the cells with the sample solution. The syringe was inserted at a slow twist into the bottom well of the cell and the liquid was forced upward at a slow rate in order to avoid the accumulation of air bubbles. The rise of the liquid level was observed and the action continued until the cell was completely filled. The stoppers were then replaced and the cell carefully washed before the run.

Reference Beam Compensation

The samples could not be studied without solvent compensation in the reference beam. All the solvents used have strong absorption bands in the special range of interest. Hence double-beam method of spectrum determination was followed throughout. Matched pairs of cells were used throughout.

Visible and U.V. Determinations - In the UV-Vis spectrophotometry the Double-beam technique was used. The samples were not found to be fluorescent in the spectral range of interest. The pyridine derivatives as solvent

could not be used below 400 milimicrons because of strong solvent absorption. In all the measurements 1 cm quartz-cells were used. For each solvent measurements were taken to get an almost flat I_0 line i.e., 100 percent transmission line. As in the IR study, transmission techniques were used. In the determination of the formation constants, the Perkin-Elmer 350 was used as a UV spectrophotometer.

Spectrophotometric Determination of formation constants:-

For the determination of the formation constants of the adducts between the DEHPA and the heterocyclic bases, the absorption spectra and equilibrium constants were determined at room temperature. Throughout the experiments 1 cm cells were used. The concentration of vanadium compound in the prepared solution was 0.5 percent, with the vanadium concentration being 0.0072 gramme - atoms per litre. In the determinations the transmissions were determined, which were then converted to the absorbance from the supplied table. The transmissions were determined at 340 millimicron for beta-Collidine, 354 for 4-isopropyl pyridine, 350 millimicron for 4-Benzyl pyridine, and at 346 millimicron for 4EP.

The Graddon and Wattons²¹ formula for calculating the amount of adduct formation was used. Equilibrium concentrations were calculated assuming

a linear relationship between the observed absorbance and the molecular fraction of the V (IV) present as adduct.

$$[\text{Adduct}] = [\text{total V (IV)}] \times \frac{E - E_0}{E_\infty - E_0}$$

where E is the experimental values of absorbance for the sample and the E₀ the correction for the absorbance for the pyridine itself. The E_∞ is the theoretical value of absorbance for complete adduct formation. The value of E_∞ was found by trial and error, and was taken as the value that gives the most reproducible values of the equilibrium constant.

The complete experimental data are given in the table. The average values were obtained from at least 15 determinations. The formation constants were determined with the relationship:

$$K = \frac{[\text{adduct}]}{[\text{chelate}] [\text{base}]}$$

CHAPTER IV

SYNERGISM AND PROPOSED MODELS FOR V (IV) EXTRACTION BY DEHPA WITH AND WITHOUT ORGANIC LIGANDS

Synergism

Since this work is concerned with the problem of synergism, it is appropriate to summarise this phenomenon in this section.

In the solvent extraction of metals by a mixture of two organic solvents, there may arise two ways in which the system might react, (1) one of the solvents participates in the extraction, whereas the other is inert, (2) both of the solvents participate in the extraction. In the second case the overall extraction might be higher than the sum of the extractions exhibited by the solvents alone. This is known as synergism, first noticed by Blake²³.

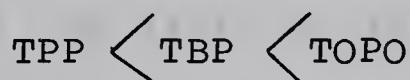
Synergic Systems

The synergic systems being studied extensively in recent years fall into two well defined categories (1) a chelating agent like TTA and a solvating agent such as TBP etc., (2) a dialkyl phosphoric acid (HX) and a neutral phosphorous ester.

1. System chelating agent/solvating solvent: Irving and Edginton^{24,25,26}, noted increased extraction of the order of 10^3 - 10^4 with a mixture TTA-TBP and

TTA-TBPO in the extraction of uranium (VI). The extracted complexes were shown to have the composition $\text{UO}_2\text{X}_2 \cdot \text{TBP}$ and $\text{UO}_2\text{X}_2 \cdot \text{TBPO}$, from infrared and isopiestic measurements. The studies were later extended to plutonium (VI), Americium (III), Europium (III) and thorium (IV).

Healy²⁷ has also reported the synergism for uranium (VI), thorium, rare earths, actinides and alkaline earths using TTA in conjunction with organophosphorous esters like TBP, TOPO and TPP. The complexes formed in the organic phases have the compositions $\text{Th}(\text{TTA})_4\text{S}$, $\text{Ca}(\text{TTA})_2\text{S}$, $\text{UO}_2(\text{TTA})_2\text{S}$, $\text{UO}_2(\text{TTA})_2\text{S}_2$ etc. In all the compounds the S denotes the organophosphorous ester. Healy showed that the synergism depends on the basicity of P=O bond, the synergism increasing with the increasing basicity of P=O bond, in the order



Recently it has been reported that synergism is possible with many other organic compounds besides the organophosphorous compounds. These include the alcohols like n-decyl alcohol, ethyl hexyl alcohol (EHA), ketones like methyl isopropyl ketone, amides such as N-butyl acetanilide (BAA)²⁸. The extracted species have been given similar formulas as in other cases - $\text{Th}(\text{TTA})_4 \cdot (\text{EHA})$; $\text{Am}(\text{TTA})_3 \cdot (\text{EHA})_2$

$\text{Am}(\text{TTA})_3 \cdot (\text{MIK})_2$, $\text{Th}(\text{TTA})_4 \cdot \text{BAA}$, $\text{UO}_2(\text{TTA})_2 \cdot \text{BAA}$, to mention a few. As pointed out earlier synergism has been reported also for the extraction of $\text{Cu}(\text{II})$ by acetyl acetonate in the presence of pyridines^{19,20}. The extracted complex has a composition similar to those shown above.

2. System dialkyl phosphoric acid/neutral phosphorous ester: Some important examples in this system are di-2-ethyl hexyl phosphoric acid (DEHPA) - TBP^{23,29,30}, mono-2-ethyl hexyl phosphoric acid (H_2MEHPA) - TBP³¹, dibutyl phosphate (DBP) - TBP³² and DBP - TOPO^{31,33}. As in the case of other systems, the synergism was shown to be dependent on the $\text{P}=\text{O}$ bond basicity.

The effectiveness increased in the series -

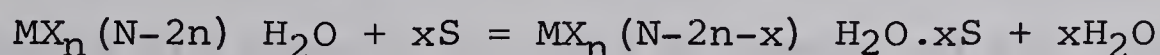
$(\text{RO})_3\text{PO} < \text{R}(\text{RO})_2\text{PO} < \text{R}_2(\text{RO})\text{PO} < \text{R}_3\text{PO}$
phosphate phosphonate phosphinate phosphine oxide.

Synergism has been reported as indicated earlier for $\text{U}(\text{VI})$, $\text{Pu}(\text{IV})$, $\text{Pu}(\text{VI})$. In each case it was noted that synergism increased with increased concentrations of S to a maximum, and then decreased. This behavior was attributed to increasing interaction between two solvents. Vanadium (IV), V (V), Al (III), Mo (III), Fe (III), Ti (III) and Th (IV) did not show synergism with organo phosphorous acids.

Mechanism of Synergism

Though the phenomenon of synergism has been widely studied, its mechanism is not fully explained. The complexity of the problem has been aggravated by such unsolved problems such as the role of water, inert diluent and possible changes in coordination and solvation. There are also possible effects resulting from changes in dielectric constant and self association in one of the solvents on the introduction of the other.

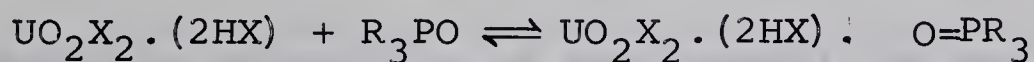
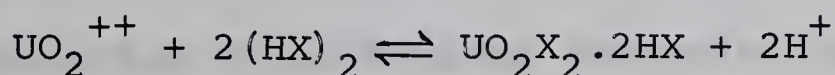
Irving and Edgington^{25,26} postulated that synergism primarily depends on a mechanism in which the molecules of water which are attached to the neutral chelated complex MX_n are replaced by a hydrophobic group S. They also state that the maximum co-ordination number of the metal and geometry of the ligands should be favourable. The reactions by which this can arise have been generalised by the equation -



where X is the bidentate ligand and N is the maximum co-ordination number of metal M. Synergism can occur as long as the chelate is co-ordinately unsaturated i.e., $n < N/2$. When $n = N/2$, synergism cannot occur. Irving and Edgington's postulates have been substantiated in the case of plutonium (V), neptunium (V), thorium (IV), neptunium (IV), plutonium (IV) and others.

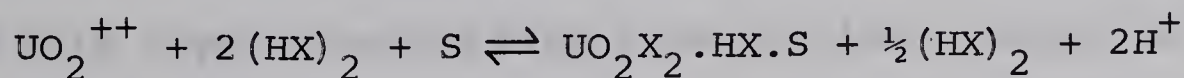
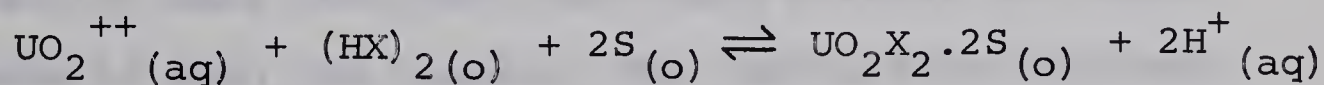
The postulates of Irving and Edgington were in general substantiated by the isolation of synergistic complexes from the organic phase by Healy, with the expected M/TTA/TBP ratios for thorium and uranium. The model was further substantiated by Healy and Ferraro³⁴ who confirmed the composition of synergistic complexes of uranium and thorium salts of TTA with TBP, TOPO and BAA.

Blake et al²³ suggested a mechanism for synergism involving organophosphorous acid and neutral organophosphorous compounds. They thought that the synergism arises from the reaction:



where in the synergistic complex, the co-ordination number of UO_2^{++} ion is raised.

Kennedy and Deane³⁵ proved that organophosphorous compounds are dimeric in inert diluents, so the probable reaction should be represented by:



The equation represented explained the formation of synergistic complexes of uranium e.g. $\text{UO}_2(\text{DBP})_2 \cdot 2(\text{TOPO})$ and $\text{UO}_2(\text{DBP})_2 \cdot \text{HDBP} \cdot \text{TOPO}$.

It has been pointed out by Kennedy and Deanne³³

that it is possible that either one or two of the solvating HX molecules may be replaced by S to give synergistic complexes according to the strength and concentration of S. Thus dibutyl phosphate and TBP give $\text{UO}_2\text{X}_2 \cdot \text{HX} \cdot \text{S}$ in CCl_4 and diamyl phosphate gives $\text{VO}_2\text{X}_2\text{S}^{36}$ in Xylene³⁵.

T. Sato³⁰ showed from IR studies that TBP is possibly attached to DEHPA by hydrogen bonding in the uranium extraction in the $\text{UO}_2^{++}/\text{DEHPA}/\text{TBP}$ system.

From the above resume it seems that no complete explanation is yet possible. In fact it might happen that synergism can occur by any one mechanism or a combination of mechanisms depending on conditions.

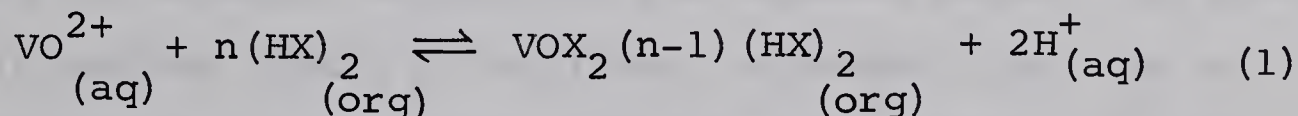
B. Model of Extraction of the Vanadyl Ion by DEHPA & Ligands

Since the published literature showed little reference to the extraction of V (IV) by DEHPA, a mechanism of extraction was lacking. Certain clues pointing to the mechanism of V (IV) extraction were found from extraction data obtained from tests without any added ligands in both the phases. The indications obtained from this type of extraction gave further insight to the study of the extraction mechanism in the presence of ligands in the organic phase.

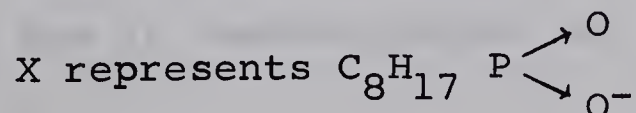
From the foregoing section, the main condition for synergism appears to be the direct bond formation

between the central metal ion and the ligand when the metal is co-ordinately unsaturated, or that the extracted species undergoes a replacement reaction with the synergistic agent. Such considerations when applied to the extraction of V (IV) necessitate the definite indication that the V (IV) ion does not exist in the polymerised state in either the aqueous, or organic phase. Also a definite indication of the number of molecules of DEHPA involved in the extraction of V (IV) is a must, as it is known from the extraction studies of other ions that the number of molecules of extractant needed might exceed that indicated by the ionic charge due to co-ordination by the extractant itself.

Considering the fact that the extracted species must be an uncharged species the following equation is proposed for the extraction of V (IV) by DEHPA (HX).



The equation has been proposed on the assumption that the vanadyl ion is a monomer in the aqueous phase. The coefficient, n, has to be determined by solvent extraction data. A dimeric formula has been used for DEHPA, in consequence of the proposition of others³⁵, that in diluents of low dielectric constants the organophosphorous acids exist as dimers.



The equilibrium constant of the above equation can be written as

$$K = \frac{[\text{VOX}_2 \cdot (n-1) (\text{HX})_2]_o [\text{H}^+]_{\text{aq}}^2}{[\text{VO}^{++}]_{\text{aq}} [(\text{HX})_2]_o^n}$$

$$\frac{[\text{VOX}_2 \cdot (n-1) (\text{HX})_2]_o}{[\text{VO}^{2+}]_{\text{aq}}} = D$$

where D is the experimentally determined extraction coefficient.

We have:

$$K = \frac{D [\text{H}^+]^2}{[(\text{HX})_2]^n}$$

So that at constant $[\text{H}^+]$

$$K^1 = \frac{D}{[(\text{HX})_2]^n} \quad (2)$$

Hence at constant acidity in the aqueous phase, the plot of D against $[(\text{HX})_2]^n$ will be a straight line, the n which gives the straight line gives the number of $(\text{HX})_2$ molecules for the extraction. In order to conduct this experiment the $[\text{V}]$ must be much lower than $[\text{DEHPA}]$. It is to be assumed that the concentration of $(\text{HX})_2$ remains constant throughout the extraction. It is to be noted that n-1 gives the number of molecules of $(\text{HX})_2$ which is bound to the VOX_2 by adduct formation.

Now if concentrations of $(\text{HX})_2$ and VO^{2+} are kept

constant with $[VO^{2+}]$ much lower than the $[(HX)_2]$ we get:

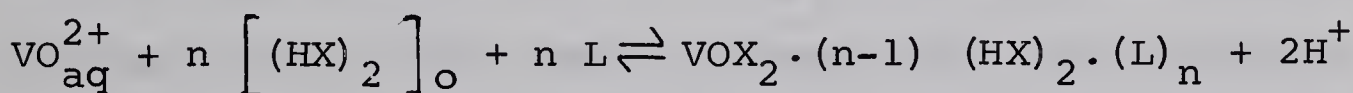
$$C = D(H^+)^2$$

where C = a constant which after taking logarithms becomes

$$\log D = 2 \text{ pH} + \log C \quad (3)$$

Hence the extraction coefficient is related with the pH of the solution by a logarithmic function. The equation will represent the experimental data only if the monomeric species of the vanadyl ion is present in the aqueous phase.

In the extraction of VO^{2+} in the presence of ligands in the organic phase, where it might be assumed that the interaction between the ligand (second solvent) and the extracted species $VOX_2 \cdot (n-1) (HX)_2$ complex gives rise to the synergistic effect, we can write the equation:



where L = ligand

So for equilibrium conditions

$$\frac{[VOX_2 \cdot (n-1) (HX)_2 \cdot (L)_n] [H^+]^2}{[VO^{2+}]_{aq} [(HX)_2]_o^n \cdot [(L)]_o^n} = K^1$$

$$\text{or} \quad \frac{D [H^+]^2}{[(HX)_2]_o^n [L]_o^n} = K^1$$

If $[H^+]$ and $[(HX)_2]$ are kept constant, which approximately holds for low concentration of VO^{2+} ion in the aqueous phase, it follows that:

$$\frac{D}{[L]^n} = K, \text{ or } D = K [L]^n$$

Therefore if any synergistic effect occurs in the presence of pyridines or amine derivative, the plot of D vs $[L]^n$ will give a straight line, the n which gives the straight line is the number of molecules of ligand (L) which forms the synergistic complex or adduct.

Before one can test the above postulated mechanisms of vanadium (IV) extraction, the qualitative effect of various ligands such as chloride, nitrate and thiocyanate ions in the aqueous phase have to be known, in order to find the extent to which they effect the extraction of V (IV). The ligands, chlorate and CN^- , could not be used because of rapid oxidation of V (IV) by the chlorate ion, and the formation of an insoluble cyanide complex.

CHAPTER V

DISCUSSION OF THE EFFECT OF ANIONS NO_3^- , Cl^- , SCN^- ON THE EXTRACTION OF VO^{2+} BY DEHPA

A. Dependence of the extraction of VO^{2+} ion on the concentration of VO^{2+} ion in the aqueous phase

These extractions were done to get preliminary information as to the nature of VO^{2+} ion in the aqueous phase. For this series of extractions the equilibrium pH value and DEHPA concentration were kept nearly constant. To approximate the ideality of the VO^{2+} ion in the aqueous phase, a dilute solution was employed for extraction. On examination of the data (Fig. 1) it is found that the extraction coefficient is generally high. Now the distribution coefficient can be represented by the equation:

$$D = K [\text{HX}]^m \frac{(\gamma_{\text{HX}})^m \gamma_{\text{M}^{n+}}}{\gamma_{\text{MX}_n}^{\circ}} \quad m \geq n$$

This equation holds if the ion exchange mechanism for the extraction is assumed. In the equation, K is the equilibrium constant of the extraction reaction, $\gamma_{\text{M}^{n+}}$ is the activity coefficient of the VO^{2+} ion in the aqueous phase, γ_{HX} is the activity coefficient of DEHPA in organic phase, and $\gamma_{\text{MX}_n}^{\circ}$ is the activity coefficient of the extracted species in the organic phase. Since the equation is applicable to the mononuclear species of V (IV) in the aqueous phase, the extraction should not

depend on the aqueous phase concentration of the metal ion when this stipulation is valid. Unfortunately there are a few difficulties in testing the validity of the equation. The major difficulties are (1) the necessity of maintaining $\gamma_{M^{n+}}$, the activity coefficient of the metal ion, at a constant value, (2) to keep the activity coefficient of HX at a constant value, as the increasing concentration in the organic phase of the extracted species is expected to change this coefficient, (3) that the pH has to be kept constant within reasonable limits. Without the use of buffers in the aqueous phase, the above requirements could be met only at a very low concentration of the metal ion. Concentrations of the order of 10^{-19} to 10^{-13} molar are desirable. These concentration ranges have been used by various workers to establish the general validity of the expression. The validity of these assumptions has been shown for cobalt, cerium and iron extractions³⁸⁻⁴². The data (Table I, Fig. I) shows that the distribution coefficient is approximately constant over the initial concentration ranges. The observed deviations can be attributed to the relatively high concentration of V (IV) used in this extraction (10^{-3} to 10^{-2} M). Although the ideality of the solution cannot be maintained for the organic and aqueous phases, the data indicate that the mononuclear species should be involved in the extraction process

over this pH range, aqueous phase V (IV) concentration and extractant concentration. The extraction coefficient vs V (IV) concentration plot shows a broad hump for some of the N series, which indicates that the extraction is nearly constant over the range of the crest. This might be expected because the activity coefficient contributions from the salt in the organic phase and the metal species in the aqueous phase will cancel each other to give a factor of unity, since the activity coefficients γ_{HX} , $\gamma_{M^{n+}}$ and γ_{MX}^O are all expected to change with the changing metal ion concentration in both the aqueous and organic phases. The N₄ extraction data show higher extraction coefficients. In this case the initial pH is 2.3 and the final pH is 2.0. The extractions were carried out up to 7×10^{-3} molar V (IV) concentration in the aqueous phase. The high extraction can partially be explained by the high concentration of DEHPA used. However the extraction, when compared to the extraction by 0.2 and 0.3 molar DEHPA where the DEHPA to V (IV) proportion is almost the same order, points to the fact that the activity coefficient changes are also involved.

B. Dependence of extraction on the chloride ion concentration

These extractions are indicated by the A series of data (Table XII, Fig. 2). A¹ series of extractions

were carried out at various HCl concentrations. The concentrations were varied because the extraction mechanism may be different with a high HCl concentration. It was felt that a complex of the form, H_2VOCl_2 , might extract into the organic phase. The P=O bond of the extractant, due to its basic character, might form an adduct of the type $(H_2VOCl_2) \cdot (HA)_n$. Data shows that these expectations were not realised, even if a complex of the type indicated was formed. The fact that there is a complex formation in the aqueous phase is indicated by a change in color of the aqueous stock solution after 24 hours or more. Hence, even if the complex is formed, the extractant cannot extract effectively by solvate formation of the complex, as demonstrated for $FeCl_3$ extractions by ethers at high HCl concentrations⁴³. The other data for the A series extractions were for KCl base solutions instead of HCl base solutions. KCl was used to avoid high concentration of hydrogen ions in the aqueous phase, which will tend to decrease the extraction coefficient. The extraction coefficient for all the A^2 to A^5 series decreases almost uniformly with the rise of Cl^- ion concentration (Fig. 2).

The decrease in the extraction coefficient can be explained by the formation of the vanadyl complexes in the aqueous phase. The complex, if formed, should be inextractable with di-2-ethyl hexyl phosphoric acid by the usual ion exchange mechanism. The increase of the

Cl^- ion concentration will form more of the complex anion, making the vanadium more and more inextractable. Hence the extraction coefficient will decrease. Proof that the complex is actually formed is indicated by a change of color of the aqueous phase after standing for a few hours. The nature of the complex is not known definitely⁴⁴ nor the value of the stability constants. The extraction studies may be used in this particular case to find out the kinetic parameters, since a calculation can be made for the amount of complex formed with the passage of time.

C. Dependence of extraction on the thiocyanate ion concentration

The thiocyanate ion is a very important inorganic complexing agent. The thiocyanate complexes can be extracted in the organic oxygen carrying solvents. The extraction of the metals is based on the solubilities of the thiocyanate complexes in the organic phase. A very comprehensive study of thiocyanate complex extractions for ethyl ether has been done by Bock⁴⁵. He has shown that for vanadium (IV), the extractibility decreases with the increase of the ammonium thiocyanate concentration in the aqueous phase. He has also shown that for each metal ion there is a particular optimum thiocyanate concentration for good extraction. No data is available, except for TBP, for the organo phosphorous

compounds, TBP being used as a solvent for iron removal as a thiocyanate complex in the analysis of steel⁴⁶.

The object of this particular study was to find out the effect of thiocyanate ion on the V (IV) extraction by DEHPA. The data of Table XIII represents these extractions. In general, the extraction coefficient decreases with increasing thiocyanate ion concentrations. The extractions were carried out with 0.01 M vanadium (IV) solutions and various concentrations of the thiocyanate ion concentrations. The data is plotted (Fig. 3). The plot shows that with increasing concentrations of the thiocyanate ion, the extraction coefficient tends towards a limiting value, even if the different initial pH values are used. For the B¹, B², and B³ series of extractions, the optimum initial pH seems to be 3.1. The decrease of the extraction with the increase of the ammonium thiocyanate concentration is to be attributed to the increased formation of thiocyanate complexes in the aqueous phase. The actual complexes present might have compositions depending on the concentration in the aqueous phase. With a low concentration of the thiocyanate, the extraction coefficient is much increased, as shown by the data B⁴. In this case a maximum distribution coefficient of 52 is obtained, which is quite high. At low concentrations and at 1:1 molar ratios of V (IV) and CNS⁻, the complex

$[\text{VO}(\text{CNS})]^+$ might be formed, which should be more extractable than the complexes of the type $[\text{VO}(\text{CNS})_2]^{--}$ which have a double negative charge and thus will be best stabilized in the aqueous phase. Further intensive work is required for mechanism study, which was not pursued by the author. The data show that the thiocyanate ion seriously interferes with the extraction process as a whole.

D. Dependence of Vanadium (IV) extraction on nitrate ion concentration

The extraction of metallic ions from nitrate medium has been conducted for many rare earth elements⁴⁷. In all cases the extraction increases with nitrate concentration. The extractants in all cases were neutral organic solvents. Few references are found for works carried out with acidic extractants together with the nitrate medium. A recent paper by C. J. Hardy⁴⁸ describes the results obtained by the mono and dibutylphosphoric acid extraction of zirconium from nitrate solutions.

The data obtained for vanadium (IV) extraction from nitrate medium is given in Table XV. From the results it is found that NaNO_3 concentrations between 1 to 5 molar are highly effective in increasing the extraction coefficient from 0.01 M V (IV) solutions. The C^2 series of experimental data shows that extraction coefficients as high as 95 can be obtained by increasing

the concentration of nitrate. The high extraction shown in the presence of nitrate ions is difficult to explain (Fig. 4(a), 4(b) and 4(c)).

It was thought that the high extraction may be due to a salting-out effect. This assumption necessitates that there is a considerable amount of vanadyl complex of DEHPA dissolved in the aqueous phase which is not extracted in the organic phase. The introduction of NaNO_3 lowers the activity of H_2O , hence the dissolved chelate compounds should be no longer thermodynamically stable in the aqueous phase due to a lower state of solvation and the big organic complex is pushed into the organic phase to maintain a new equilibrium constant. The presence of appreciable amounts of chelate complex in the organic phase is a necessity for proving this assumption. Tests showed that the prepared vanadyl complex is totally insoluble in water. Hence the foregoing assumptions for the salting-out effect for vanadyl species do not hold. The possibility of the existence of a nitrate complex in the organic phase was ruled out because tests did not show the presence of nitrogen in the organic phase. Tests did show the presence of sodium in the organic phase. The sodium has been shown to be extracted by DEHPA⁴⁹. The extracted species has been reported as $\text{NaX} \cdot 3\text{HX}$. It is possible that this might interact with the vanadyl species to give a new species

whose formation depends upon the salting out of $\text{NaX} \cdot 3\text{HX}$. It is seen from the data that there is a gradual decrease in pH which complicates the picture. Further work is required to explain this increase in extraction.

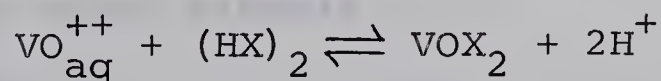
CHAPTER VI

DISCUSSION (II) OF THE SOLVENT EXTRACTION DATA - MECHANISM OF EXTRACTION AND SYNERGISM

In the following paragraphs the solvent extraction data will be discussed.

A. Dependence of the extraction coefficient on the DEHPA concentration in the organic phase

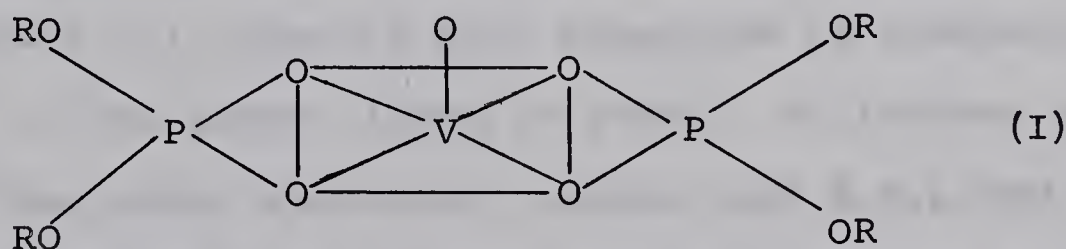
The results for these extraction studies were plotted to give the curves in Fig. 5 and Fig. 6. It is found that the straight line relationship is obtained between the extraction coefficient and the first power of $[\text{DEHPA}]_2$ concentration in the organic phase. The slope of the straight lines depends on the equilibrium constant of the extraction reaction and the hydrogen ion concentration of the solution. As the straight line relationship clearly establishes that the extraction coefficient depends on the first power of the DEHPA concentration in the organic phase, the proper chemical equation for the extraction of VO^{++} ion is



In this case VOX_2 is a chelated complex which does not form any adduct of the type $\text{VOX}_2 \cdot (\text{HX})_2$. This is striking in view of the fact that the uranyl complexes of DEHPA and other organophosphorous acids and the

complexes of uranyl ion with thenoyltrifluoro acetone, have been shown to be of the type $\text{UO}_2\text{X}_2 \cdot (\text{HX})_2$, where X represents the organic part of the respective chelating agent.

The formation of the neutral complex VOX_2 , suggests that the complex will have less possibility of forming an adduct of the type, $\text{VOX}_2 \cdot \text{B}$, where B is a neutral organophosphorous compound. This is supported by the earlier report that the vanadium (IV) does not show synergistic extraction with organophosphorous compounds. If there were any adduct formation to give a complex of the type, $\text{VOX}_2 \cdot (\text{HX})_2$, the replacement of $(\text{HX})_2$ by more hydrophobic organophosphorous compounds would show synergistic extraction, and in that case the extraction would have increased with increasing concentration of neutral organophosphorous compounds. Since the extracted species should be neutral, we can tentatively write the structure for the vanadium (IV) - DEHPA complex as shown below. This complex is analogous with the acetyl acetate complex of VO^{2+} even though the structure is to be verified by other methods.



R = Di-2-ethyl hexyl radical.

Incidentally it has been mentioned that in the

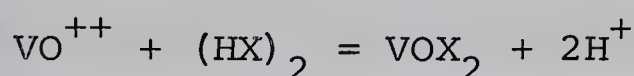
extraction of V (IV) by DEHPA the extractions are considerably increased by a high concentration of NaNO_3 in the aqueous phase. On analysis of the organic phase obtained after the extraction of V (IV) by DEHPA in the presence of NaNO_3 in the aqueous phase, it was found that the organic phase does not show the presence of NO_3^- . Hence the increased extraction may be attributed to the salting-out effect of $\text{NaX} \cdot 3\text{HX}$ which interacts with the V (IV) species in the organic phase. The indication of the presence of neutral complex (I) is in agreement with this view, since we have no other idea how this increased extraction can occur in the presence of nitrate ions.

The failure of the formation of the adduct $\text{VOX}_2 \cdot (\text{HX})$ or $\text{VOX}_2 \cdot (\text{HX})_2$ may be due to the low co-ordinating power of P=O group in the DEHPA molecule. The same argument might hold for organophosphorous compounds in which P=O bond exists. The lower electropositive character of the V-atom might also be responsible for the inability of adduct formation. The assumption of the structure (I) suggests that synergism is theoretically possible, if the proper ligand is found. To further substantiate the above structure, optical and E.P.R. and IR study of the extracted complex was done. These studies are discussed in subsequent chapters.

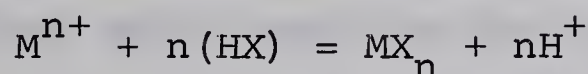
B. Dependence of the V (IV) extraction on the H^+ concentration in the aqueous phase

A study was made to establish the exact nature of the dependency of the extraction on $[H^+]$. Fig. 7 shows a plot of the log extraction coefficient versus pH.

The plot gives a straight line with a slope of + 1.5 when DEHPA concentration is 0.4 mol. If the extraction proceeds according to the mechanism,



the slope of the straight line should be + 2.0. The closeness of the experimental value indicates that the mechanism is correct. In general for an extraction of the type



the equilibrium constant should be given by

$$K = \frac{(MX_n) (H^+) \gamma_{MX_n} \gamma_{H^+}^n}{(M^{n+}) (HX)^n \gamma_{M_n} + \gamma_{HX}^n}$$

Unfortunately the literature⁵⁰ only shows that the above relationship is found to be not exactly true. Most of the literature data have been correlated with the relationship:

$$K^1 = \frac{(MX_n) (H^+)^x}{(M^{n+}) (HX)^n}$$

where x is usually lower than the expected theoretical value of n. This discrepancy has been attributed to the non-ideality of the aqueous phase solutions in the

presence of various ions.

The calculation of the equilibrium constant from the slope of the straight lines obtained from the plot of the dependency of extraction on the DEHPA concentration gave the value for K of 0.10. The value calculated from the data of pH dependency of extraction gave a value for K of 0.195. The closeness of these two values indicates that the basic model of extraction should be correct.

The low value obtained for the equilibrium constant is a factor which is responsible for the lower extraction of VO^{++} from the aqueous phase. The values of K for uranium extraction by different extractants are very much higher which explains the relatively high extraction coefficients for uranium⁷⁷.

Anomalous Extraction of V (IV)

An interesting phenomenon in the extraction of V (IV) by DEHPA is the change of slope of the extraction coefficient vs the pH curve for the lower concentrations of DEHPA (Fig. 8 and Fig. 7). The plot of extraction coefficient versus pH is a straight line in the case of extraction by 0.4 Molar DEHPA, but the extraction with DEHPA of concentration 0.05 M shows that the slope decreases as the pH is increased even though

the V (IV) concentration compared to DEHPA was small in each case. Since this slope change was not found in the earlier study of the pH dependency of the extraction, several runs were made to establish the nature of extraction at pH's higher than 4 which is the precipitation point for vanadyl sulfate.

For this purpose, it was necessary to have an aqueous solution of V (IV) of a definite pH. The condition was met by the preparation of stock solutions with sodium acetate - acetic acid buffer. The acetate concentration was kept at a constant concentration of 0.2 molar, to insure that there is no change in the ionic strength. These extraction data are plotted in Fig. 8. It was found that these plots show a maximum extraction coefficient near a pH of 4.0. The extraction rises steeply, reaches a maximum, and then falls off very sharply.

It is interesting that other workers have observed that maximum extraction of V (IV) is obtained at a pH of 4 when TTA is used as an extractant⁵¹. Unfortunately a detailed study to elucidate this phenomena with TTA extraction was not made. The occurrence of the same phenomenon, in both the DEHPA extraction and TTA extractions, must be due to the inherent chemical change in the aqueous phase. In the absence of adequate data on the state of V (IV) ion at high pH levels, only guesses

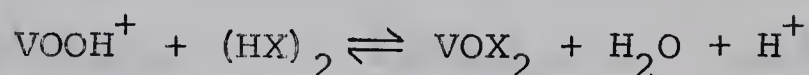
can be made.

The following qualitative explanation is offered for the phenomena. It is well known from the general principles of solvent extraction chemistry that any charged species is thermodynamically unstable in the organic phase, since charged species are not expected to be solvated by a solvent of low di-electric constant. Solvation makes the ion thermodynamically stable in the aqueous phase. If there is the formation of any charged species in the aqueous phase other than the VO^{++} aq. ion, it becomes unlikely that the species will be extracted by the DEHPA or TTA. A natural consequence of chelation is that the charges must be neutralised for the extraction to occur. Therefore one can say that the species which extracts is still the neutral chelate complex. At high pH levels, the formation of these complexes is hindered because of the increase of $[\text{OH}^-]$. It is noteworthy that the vanadyl ion precipitates at a pH of 4 - 4.2⁴⁴. There is a possibility that the OH^- ion forms an aqueous species of the type indicated in the equation



An ion of the type, VOOH^+ , might be more hydrophilic in view of the presence of one hydroxyl group. Since this reaction will be expected to compete with the chelation reaction, the available VO^{++} for chelate formation is reduced. But there is a possibility that

with a high concentration of DEHPA even the vanadium ion of the type VOOH^+ will be extracted by the simple mechanism of salt formation from hydroxylated vanadyl ion and DEHPA.



That this possibility is indeed realized is shown by the rise of extraction with increase in the concentration of DEHPA. The maximum or peak heights increase with an increase in DEHPA.

If the hydroxyl ion is regarded as a complexing agent, the metal complexes involving them must also appear in the distribution ratio. Since such complexes are soluble only in the aqueous phase one can write⁴³

$$D = \frac{(\text{MX}_n)_o}{\sum_{i=0}^p \sum_{j=0}^q \text{MX}_i \text{L}_j}$$

$$= K \left[\frac{(\text{HX})_o^n}{(\text{H})^n} \right] \left[1 + \sum_{i=0}^p \sum_{j=0}^q K_{\text{MX}_i \text{L}_j} (\text{X})^i (\text{L})^j \right]^{-1}$$

If the hydrolysis is regarded as a special case of complexing, and if there is no chelate formation in the aqueous phase, the above general equation for the dependence of the extraction coefficient, D , on the concentration of ligand can be simplified for constant $[\text{HX}]_o/[\text{H}^+]$. The differentiation of $\log D$ with respect to $\log L$ then gives

$$\frac{\partial \log D}{\partial \log (L)} = n - \bar{I}$$

where \bar{I} is the average number of ligands per metal atom in the aqueous phase. Since L is OH^-

$$\frac{\partial \log D}{\partial \log (\text{OH}^-)} = - \frac{\partial \log D}{\partial \log (\text{H}^+)} = \frac{\partial \log D}{\partial \text{pH}} = n - \bar{I}$$

since $\frac{\partial \log D}{\partial \text{pH}}$ gives the slope of the extraction coefficient versus pH curve, the slope will gradually decrease to zero as \bar{I} approaches n . The behavior can be explained by this reasoning even after the peak is attained.

Since the D vs pH curves in Fig. 8 qualitatively approaches the theoretical expectation of the above equations, it can be assumed that vanadium (IV) ion exists as a hydrolysed species in moderately acidic solutions. The proportion of hydrolysed species increases with increase in pH. This will explain the anomalous extraction of V (IV) by TTA and DEHPA.

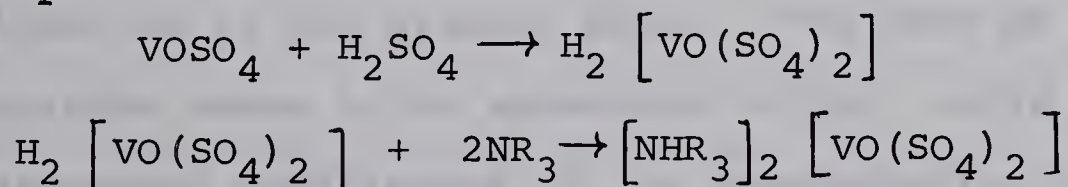
C. Effect of Tri-isooctyl amine on the V (IV) extraction by DEHPA

The extractions were done to find the possibility of combined extractions of V (IV) by DEHPA and tri-isooctyl amine. The tri-isooctyl amine was selected as it was studied by many workers in solvent extraction fields⁵². The results of the extraction study are represented in Fig. 9. It is seen from the figure that

the extractions continuously decrease as the amount of tri-isooctyl amine in the organic phase increases. The study of the effect of pH on the extraction shows that the extraction does not increase with the decrease of pH. The finding is in direct contrast to that found in the extraction of thorium by a mixture of thenoyl tri-fluoro acetone and tri-normal octyl amine⁵² and to that found in the extraction of uranium (IV) by alkyl amines⁵³. In the case of extractions with TTA and tri-n-octylamine, the tri-n-octylamine is thought to act as a synergistic agent, and there is increased extraction with the addition of tri-n-octylamine. The increased extractions were supposed to be due to the formation of the complex $\text{ThT}_4\text{R}_3\text{NHCl}$, where Th represents the thenoyl influoro acetone part and R_3NHCl the amine hydrochloride portion. The formation of such complexes must be ruled out in the case of DEHPA plus tri-isooctyl amine extraction of V (IV). The decrease of extraction may be explained on the basis of a strong interaction between the DEHPA and tri-isooctyl amine in the organic phase. As a matter of fact, it was found in the course of the tests that tri-isooctylamine forms a semi-solid compound with the addition of DEHPA. Hence it is likely that the salt formation reaction competes with the extraction reaction, thereby decreasing the extraction with increasing proportion of the amine. It seems that the salt formation with DEHPA is much more favored than the

chelation reaction. The extractions also suggest that the possibility of the adduct formation between the chelated complex of V (IV) and DEHPA and the salt of DEHPA and tri-isooctylamine is less. The formation of $\text{ThT}_4 \cdot \text{R}_3\text{HNCl}$ in the case of thorium might be attributed to steric facility. The adduct formation in the case of V (IV) should be difficult, as it was found earlier that the chelate complex of V (IV) and DEHPA does not add another molecule of DEHPA as a simple ligand. In this case the salt formation makes the situation much worse because the V (IV) would have to accommodate a much larger ligand.

Lowering of extraction with decrease in pH even in the presence of tri-isooctylamine in the organic phase suggests that the principal mechanism of extraction is the ion exchange extraction by DEHPA. The anion exchange extractions, which have been established in the case of high molecular weight amine extractions of uranium at high acidity, are not expected to be evident in this case. Even if such a mechanism of extraction was possible, it is likely that contribution from such a mechanism might be negligible, even if such an extraction might theoretically be possible through the following reaction steps.



Similar reactions have been proposed for the extraction of uranium by alkylamines at a very high acidity⁵³.

D. Extraction dependency of V (IV) on the concentration of pyridine derivatives in the organic phase

The five pyridine derivatives chosen for this purpose were:

- (1) 4-ethyl pyridine
- (2) 4-isopropyl pyridine
- (3) 2-benzyl pyridine
- (4) 4-benzyl pyridine
- (5) 2-(5 nonyl) pyridine

The different pyridine derivatives were chosen to see if the side chain position and length have any effect on the extraction of V (IV). Fig. 10 and 11 represent the extraction data. Fig. 11 indicates the dependence of extraction on the H_2SO_4 concentration. Since the conditions of extraction were maintained constant as far as possible, the increase of extraction over that indicated by the plot of extraction of VO^{++} by DEHPA can be attributed to the synergistic properties of the pyridine derivatives. Fig. 10 shows that for 2BP, 4EP, 4BP and 2-(5 nonyl) pyridine the extraction increases continuously with increasing concentration of Py-derivatives in the organic phase. The case of 4-isopropyl pyridine seems to be anomalous as the curve of the extraction coefficient (D) vs concentration shows a hump.

After reaching a maximum the extraction decreases very sharply.

The least effective synergistic agent seems to be the 2-(5-nonyl) pyridine. The 2BP, 4BP and 4EP show a relatively high synergistic effect. The effect of 2-benzyl pyridine would be expected to be quite low as there is a big substituent group in the 2 position in the pyridine ring as in the 2-(5-nonyl) pyridine. Since it is expected that interaction between the V (IV) atom in the chelate and the pyridine derivative would be through the nitrogen atom, the presence of large groups in the 2-position should hinder such interaction. In the case of 2-(5-nonyl) pyridine, this effect would explain the lower synergism because of the very large nonyl group. The nonyl group should be sterically highly unsuitable for the synergistic interaction. The much higher synergistic extraction of 2-benzyl pyridine is difficult to explain. In this case the benzyl group is also in the 2-position hence it should also be less active as a synergistic agent. The action of the benzyl group seems to be different from that of the nonyl group. It is proposed that the synergic extraction of pyridine derivatives occurs in the following way. The nitrogen atom in the pyridine is in an aromatic ring system with delocalised π orbitals, so that there is a possibility of transmission through the donor π atom to the ring π

system of some electron density. Hence the V (IV) atom can function as a back donor, so that there is the possibility of $6-\pi$ synergic bonding between the V (IV) atom and the pyridine derivatives. In the case of neutral organophosphorous compounds this type of $6-\pi$ synergic bonding is not possible. It is likely that this $6-\pi$ bonding is responsible for the enhanced extraction in the presence of the pyridine derivatives. In the case of benzyl pyridines there is the possibility of increased $6-\pi$ synergistic bonding due to the presence of two delocalised π orbitals in the Py-derivative which reinforces the $6-\pi$ synergistic bonding. This might be responsible for the enhanced extraction in these cases. Sterically, 2-benzyl pyridine might be arranged in a strain-free way about the V (IV) atom.

Fig. 10 shows that there is an almost linear relationship between the extraction coefficient and the first power of concentration of the pyridine derivatives (the 4-isopropyl pyridine increase linearly to a certain maximum). This linearity suggests that only one pyridine derivative is associated with each V (IV) atom. Since the slope of Fig. 11 is approximately 2.0, it is evident that the basic extraction mechanism of V (IV) by DEHPA is not changed i.e., two molecules of DEHPA are required as before. Hence we can write as a tentative chemical formula for the extracted species, $VOX_2 \cdot P$, where X is

the di-2-ethyl hexyl radical, and P the Pyridine part. Since the extraction data strongly points to the fact that there is a strong interaction between some of the pyridines and vanadium species in the organic phase, it becomes necessary to study the way in which pyridines react with the vanadyl complex. IR, optical and E.P.R. spectral studies were carried out with this objective in mind.

CHAPTER VII

INFRARED--SPECTRAL STUDY

Spectral methods have found wide application for the determination of the compositions and structures of the compounds present in solution. Such studies found little application in the past for the study of extraction mechanisms. The underlying difficulty in these studies is that the supposed complex formed in the organic phase is difficult to isolate because of instability, or that the complex has existence only in the solution.

The spectral methods are based on the fact that the interaction between two different molecules in the solution generally results in, (1) the shifting of the original absorption bands of the two molecules to new frequencies, (2) the appearance of new bands characteristic of new bonds formed, (3) a change in intensity of the bands. The spectra enable the determination of the character of the bond.

1. Infrared Absorption Spectra

Infrared spectra of P=O vibrations:- The organophosphorous compounds have been widely investigated by Infrared Spectroscopy. Consequently proper assignments have already been made to most of the characteristic absorption bands.

P=O stretching frequencies have been widely investigated by Meyrick and Thompson⁵⁴, after studying a number of organophosphorous compounds, mostly phosphonates, these workers suggest that the moderately strong band in the region $1260-1250\text{ cm}^{-1}$ region originated in the P=O stretching vibration. Gore⁵⁵ was able to show that the suggestion of 1250 cm^{-1} region for this vibration was reasonably in accord with theory. He also indicated that the region $1300-1100\text{ cm}^{-1}$ for this vibration, depends on the P=O bond length. His finding was substantiated by Daasch and Smith⁵⁶ who showed that the frequency of this vibration is determined largely by the electro negative substituents on the phosphorous atom. The frequency was shown to decrease with the decrease in the number of electro negative substituents. Phosphinates and similar materials absorb near 1240 cm^{-1} while for the compounds, biphenyl and trimethenyl phosphine oxide, the frequencies fell to 1190 and 1176 cm^{-1} .

The position of the P=O vibration was further confirmed by the work of Bellamy and Beecher⁵⁷, working with phosphates and phosphonates. This position has also been found to be true by a number of other workers⁵⁸. Bellamy has suggested the range $1300-1250\text{ cm}^{-1}$ as the range for P=O vibration. Thomas⁵⁹ has extended this range to $1350-1175$ after studying 250 organo phosphorous compounds. As indicated, the P=O frequency is primarily

dependent on the electro negativity of the substituent groups.

The P=O frequency is usually shifted to 1250-1175 cm^{-1} in molecules containing OH or NH groups^{56,57,58a,b}. In addition to the red shift the intensity of the vibration is considerably increased. In some compounds, the P=O stretching band shows a doublet structure. Gore has suggested that the doublet structure is associated with the P=O vibration itself.

V=O Bond Vibration:- It is instructive to consider the metal-oxygen vibration frequencies of other oxycations when considering the V=O stretching vibration. It has been shown that the infrared spectra of actinide ions of the type MO_2^+ , MO_2^{2+} have similar spectra⁶⁰. The most widely studied of these ions is UO_2^{++} , which shows a strong band around 930 cm^{-1} in the solid state and at 965 cm^{-1} in aqueous solution, which has been ascribed to asymmetric stretching vibration. The spectra of several uranyl-beta-diketo chelates⁶¹ shows similar vibration for UO_2 . The recent study⁶² of metal alkoxides, trialkyl silyl oxides and related silanols have been shown to have the frequencies 700-510, 1075-990 and 920-830 for M-O, C-O, and Si-O vibrations.

The case of the existence of V-O^{2+} in aqueous solution is strong, but not without ambiguity⁶³. Feltham⁶⁴ found that V (IV) has visible spectra and E.P.R.

spectra which are very similar to the solid five-co-ordinated vanadyl complexes. X-Ray diffraction studies^{65,80} of the compounds VOSO_4 and $\text{VO}(\text{acac})_2$ has firmly established the existence of VO^{2+} in solid complexes. Barrachlough⁶⁶ examined the infrared spectra of several complex compounds having metal oxygen double bonds. They reported that the stretching frequencies of metal oxygen usually can be found between 900 and 400 cm^{-1} . Specially they reported the probable V=O stretching vibration for the following compounds, VOSO_4 , 987, 1003, 1020, $\text{VO}(\text{acac})_2$ 995, $(\text{NH}_4^+)_2[\text{VO}(\text{OX})_2] \cdot 2\text{H}_2\text{O}$, 926 and $(\text{MH}_4^+)_2\text{VO}(\text{Mal})_2 \cdot 4\text{H}_2\text{O}$, 967, 977. Selbin et al.⁶⁷ determined the multiple bond frequencies of 39 V=O compounds. The spread of the V=O stretching frequency is reported as $985 \pm 50 \text{ cm}^{-1}$.

P-O-C Vibration:- The grouping P-O-C occur in many organophosphorous esters. The position of this band is assigned by Daasch and Smith⁵⁶ to 1030 cm^{-1} . The spectra⁵⁴⁻⁵⁸ of a very large number of alkyl phosphates have an extremely strong absorption band in the range 1050-995 cm^{-1} , with the great majority absorbing near 1030 cm^{-1} . Thomas⁵⁹ found that in some 300 organophosphorous compounds examined, this absorption is in the range 1050-1000 cm^{-1} for methyl and ethyl esters. In longer chain alkyl groups the frequency falls to a lower value. Thomas⁵⁹ and McIvor⁶⁸ also noted a band at 1150 cm^{-1} .

They assigned the 1030 cm^{-1} band to the P-O-(C) vibration and the higher frequency to the C-O-(P) vibration.

Metal-Ligand Vibration:- The position of metal ligand vibration is not known definitely. It has been pointed by Lewis and Wilkins⁶⁹ that in comparison with metal carbonyls and metal cyanide complexes, they should occur at around a low frequency of about 100 cm^{-1} . According to them the existence of strong bands between 200- and 600 naturally be assigned to the metal ligand stretches. Barrow⁷⁰, et al examined a number of compounds which showed the existence of strong bands between 300- and 500 cm^{-1} .

2. Infrared absorption of VDEHPA and VDEHPA in Pyridies

Infrared absorption method was applied primarily to get an insight as to the chemical structure of the complexes formed in solution. In the absence of X-Ray studies, the infrared studies were expected to give confirmation as to the chemical structure of the complex both in the adduct form or in free DEHPA form. The studies of absorption of VDEHPA were made

- (1) in benzene solution at a concentration of 1 percent
- (2) in solution in 4-ethyl pyridine, 4-benzyl pyridine, beta-Collidine, 2 ethyl pyridine and 2 benzyl pyridine.

For this study a concentration of 1 percent VDEHPA

was used. All the solutions were of different shades of blue and green.

(3) Another study was made in benzene and in hexane solutions of a mixture of 2.5 percent VDEHPA and 0.2 molar pyridine.

The use of the solution technique for the VDEHPA in spectral studies was due to the fact that the complexes of VDEHPA with pyridines could not be isolated by the method prescribed for the adducts of copper (II) beta-keto chelates with heterocyclic base²¹. The failure of the method of crystallization and evaporation was due to the fact that VDEHPA itself is a semisolid non-crystalizable substance with a high molecular weight. It is expected that the adduct, if isolated by some means, will not be solid. In fact it was found that evaporation for crystallization gave dark blue or green viscous liquids. All attempts to purify the viscous substances failed. It was found that washing the viscous substances by alcohol and acetone to remove excess bases resulted in complete decomposition. As such, it was not possible to study the adduct compounds in the solid pure state. However there is no doubt about their formation in solution with different pyridines as is evident by the formation of different colored solutions.

For the absorption studies, the solutions were made

at room temperature (20°C) and left at this temperature for complete equilibrium. Then the IR spectra of VDEHPA in solution were recorded by the IR Spectrophotometer.

The results of the spectral study are discussed as follows.

A. Spectra of VDEHPA

The spectra were recorded as shown in Fig. 12 and Fig. 13. The spectrum in Fig. 12 shows a broad band of high intensity at 1065 cm^{-1} with a doublet band of moderate intensity at $1210\text{--}1205$ and $1241\text{--}35$. There was also a band of low intensity at $880\text{--}885\text{ cm}^{-1}$. Figures 13, 16 and 17, which were recorded with a higher concentration of VDEHPA, also show bands at 1130 cm^{-1} in hexane solutions. In these figures which were obtained by scanning down to 200 cm^{-1} , two broad bands of lower intensity are seen. The low intensity bands are observed at 300 cm^{-1} and at 485 cm^{-1} , two broad bands of lower intensity are seen. The low intensity bands are observed at 300 cm^{-1} and at 485 cm^{-1} in benzene solutions. In hexane solutions similar bands were observed at 330 cm^{-1} , 490 cm^{-1} and a shoulder at 595 cm^{-1} . It is observed that in benzene solutions the two bands of low intensity which are observed in the hexane solutions are absent. They are observed at 1375 cm^{-1} and at 1440 cm^{-1} . There is a strong band at 930 cm^{-1} observable only through Perkin Elmer 421 spectrophotometers.

It was astonishing that no evidence of chemically bonded water molecules was found from the infrared spectra. The existence of water molecules in complex compounds is indicated by the presence of a band at $3650-3590\text{ cm}^{-1}$ for the free hydroxyl OH group and a band at a lower frequency for bonded groups. It is noteworthy that none of the bands are shown by the VDEHPA. It can be concluded that the complex does not contain any water molecules. During the preparation of the compound it was supposed that there are some bonded water molecules in the complex as was indicated by the deepening of blue color of VDEHPA in contact with water. It can be concluded that this deepening of color is due to the chemically non-bonded or loosely bonded water molecules which are easily removed on desiccation. It becomes evident that there is less likelihood of extraction of bonded water to the organic phase in the extraction of V (IV) by DEHPA because of the highly non-polar character of the organic phase.

The bands at $1210-5\text{ cm}^{-1}$ and at $1241-35$ are clearly associated with the P=O vibration of the complex molecule. The doublet structure of the P=O vibration is also reported by several workers. For aid in comparison with the spectra of VDEHPA, the published spectral data for several salts of DEHPA are tabulated. The published data for the IR spectra of DEHPA is also presented.

TABLE I
INFRARED ABSORPTION MAXIMA OF SEVERAL COMPOUNDS (Ref 72)

Li (DEHPA)	Na (DEHPA)	Th (DEHPA) ₄	Zr (DEHPA) ₄	Hf (DEHPA) ₄	Sc (DEHPA) ₄	UO ₂ (DEHPA) ₂
3400 (w)	3425 (m)	3160 (s)				
2944 (s)	2924 (s)	2939 (s)	2924 (Sb)	2914 (Sb)	2929 (VS)	2914 (VS)
2877 (Sh)	2877 (Sh)	2877 (Sh)	2872		2877 (Sh)	
1465 (m)	1470 (m)		1460 (m)	1460 (m)	1468 (w)	1465 (w)
1385 (w)	1385 (w)		1377 (w)	1380 (w)	1385 (w)	1380 (w)
1196 (VS)	1243 (VS)	1193 (s)	1250 (s)	1250 (s)		
		1160 (sw)	1205 (m)	1200 (m)	1210 (s)	
1102 (VS)	1100 (VS)	1090 (vs)	1150 (sh)			
			1100 (s)	1100 (Sh)	1104 (w)	1130 (s)
1035 (VS)	1053 (VS)	1057 (vs br)	1050 (vs)	1040 (vs)	1030 (vs)	1065 (vsb)
885	860 (m)	890 (s)	890 (m)	920 (m)	900 (w)	930 (m)
		770 (w)	780 (m)		770	880 (w)
		730 (w)				810 (w)
						770 (w)

TABLE II

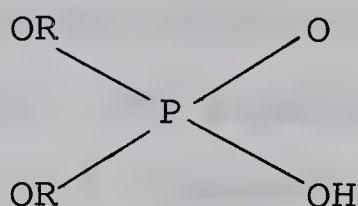
ASSIGNED FREQUENCIES OF DEHPA; DI-2-ETHYL
HEXYL PHOSPHATE (Ref 72)

Frequency cm^{-1}		Assignments
2965	(vsb)	Methyl, methylene C-H
2930	(sh)	stretching
2870		"
2750-2550	(s)	O-H stretch
broad		
2280	(sb)	" "
1680	(mb)	O-H deformation
1470		CH ₃ deformation
		CH ₂ scissor
1385		CH ₃ symmetrical deformation
1225	(s)	P=O stretching
1155	(m)	C-C-C antisymmetric stretch
1040	(vs)	P=O stretching antisymmetric
885	(m)	CH ₃ wagging vibration
-780	(w)	P=O stretch symmetric

The P=O stretching vibration of VDEHPA is in accord with the foregoing results. The doublet structure of the P=O vibration is difficult to explain in that it does not occur in all the compounds of organophosphorous acids. There is no doubt that the doublet somehow originates in the P=O bond itself⁷¹. This structure might be due to the resonance effect in the complex molecule where the double bond character is alternated between equivalent P-O bonds. Bellamy⁷¹ suggested the possibilities of rotational isomerism. The other salts of DEHPA besides VDEHPA which show the doublet structure are $\text{Hf}(\text{DEHPA})_4$, $\text{Zr}(\text{DEHPA})_4$ and thorium $\text{Th}(\text{DEHPA})_4$. The doublet structure is not reported for the $\text{Sc}(\text{DEHPA})_4$ and $\text{UO}_2(\text{DEHPA})_4$. It is likely that, not only the interaction of P=O vibration with neighboring CH groups or rotational isomerism, but the nature of the metallic cation in the complex should also be taken into account. It is possible that the P=O vibration is coupled to the other vibrations of the molecule. P=O vibration can be coupled to the V=O vibration in VDEHPA.

The identification of P=O vibration almost at the same position as in DEHPA suggests strongly the co-ordination of P=O bond to the central V (IV) nucleus. Since the VDEHPA complex does not indicate the bond for bonded O-H, it can be inferred that V nucleus is bonded to two oxygen atoms; one bond arises due to the replacement of

H^+ by one single positive charge of VO^{2+} and another bond arises due to the co-ordination of P=O bond to the central V (IV) nucleus. The oxygen atoms come from the same molecule of mono-molecular Di-2-ethyl hexyl phosphoric acid, whose structure can be represented by



The notations have been explained elsewhere.

Since the VO^{2+} ion is doubly charged positive it is reasonable to assume that V (IV) will be attached to two more oxygen atoms from the Di-2-ethyl hexyl phosphoric acid. The solvent extraction data suggested the reaction of two Di-2-ethyl hexyl phosphoric acid molecules with each VO^{2+} ion.

The band at 1065 is to be attributed to the overlapping of the POO^- stretching symmetrical vibration and the P-O-C vibration. This band does not agree well with the observations of D. F. Peppard and J. R. Ferraro⁷², who assigned the band at about 1080 cm^{-1} to POO^- stretching vibration. It is expected that there will be a considerable overlapping of bands in this region 1000-1100 for POO^- symmetrical stretching vibration, P-O anti-symmetrical stretching vibration and P-O-C vibration. Indeed that this is so is indicated by the presence of a strong band at 1125 cm^{-1} in hexane solutions. Thomas and McIvor⁶⁸ have assigned the band at

1130 cm^{-1} to C-O-(P) vibration in organophosphorous compounds so that the 1125 cm^{-1} band can be taken to arise from this vibration. The two bands observed at 1375 cm^{-1} and at 1440 cm^{-1} are of interest in that they are observable only in benzene solution. The reason for their disappearance in n-hexane solution should be attributed to the solvent itself. The possible origin for these bands, according to D. F. Peppard and J. R. Ferraro⁷², is due to CH_3 deformation and CH_2 scissor. The band at 1440 cm^{-1} has to be attributed to CH_3 deformation and that at 1375 cm^{-1} to the CH_2 scissor, according to Peppard's and Ferraro's assignment in the Table II. It is expected that in hexane solutions these vibrations of the VDEHPA are coupled to the vibration of n-hexane molecules in the solvent. In effect the vibrational intensity of the CH_2 and CH_3 groups are much diminished due to this solute and solvent coupling of vibrations. In benzene solutions the bands appear because of the absence of these coupling effects - benzene has no such groups in the molecule.

The origin of the band at 930 cm^{-1} observed through P.E. 421 I.R. Spectrophotometer is debatable. D. F. Peppard and J. R. Ferraro⁷² have assigned (Table I) this band to CH_3 wagging in Di-2-ethyl hexyl phosphate of the UO_2^{2+} ion, though they also attributed other bands of lower frequency to the same source. According to

Peppard et al, Zr, Hf and Sc salts of DEHPA also show absorption peaks near 900 cm^{-1} . The proposition of Peppard et al for the CH_3 wagging vibration seems untenable in view of the finding that in the extraction of UO_2 nitrate by DEHPA, the intensity of the band at 930 cm^{-1} is increased in the organic phase with increasing concentration of uranyl nitrate in aqueous phase, i.e. increasing extraction of UO_2^{2+} ion in the organic phase. Consequently 930 cm^{-1} has been attributed to the UO_2 stretching vibration in accordance with the finding of several other workers^{53,73}. The band at 930 cm^{-1} in VDEHPA cannot be attributed to the CH_3 wagging vibration. It has been suggested by Selbin et al⁶⁷ in the course of investigation of fifty vanadium compounds that V=O stretching vibration ranges between $985 \pm 50\text{ cm}^{-1}$. Hence in the VDEHPA complex it is reasonable to assume that any band between 900 cm^{-1} and 1035 cm^{-1} can be attributed to V=O vibration. In this connection it can be pointed out that Selbin⁶⁷ noted the existence of several absorption peaks of V=O stretch in the same compounds. Therefore it is suggested that there is the possibility of several other vibrations of V=O in the VDEHPA molecule. That this is so will be pointed out later. There is no doubt of the existence of CH_3 wagging vibration for VDEHPA. The vibration at $880\text{--}885\text{ cm}^{-1}$ (Fig. 12-18) should be

attributed to this group. This vibration is more intense in benzene solution than in hexane solution, in agreement with the previous remark that the CH_3 and CH_2 vibrations of VDEHPA will be coupled to the hexane CH_3 and CH_2 vibrations decreasing the intensity of the band. In benzene solutions the vibrations at $885\text{--}880\text{ cm}^{-1}$ have some shoulder indicating the presence of other vibrations of CH_3 wagging.

The low intensity broad bands at 330 cm^{-1} , and at $485\text{--}490\text{ cm}^{-1}$ have not been reported for any of the complexes of vanadyl ion. The origin of these bands in this region is a difficult problem to solve, but it can be suggested that the origin of these vibrations is linked with V-O (ligand) vibration. The question where the metal-ligand stretching absorbs is not settled. As pointed out earlier any band occurring between $600\text{--}200\text{ cm}^{-1}$ and of higher intensity could naturally be assigned to metal-ligand stretching. The metal ammonia ligand compounds have absorption bands in the region $300\text{--}500\text{ cm}^{-1}$. According to the suggestion of Lewis et al⁶⁹, they have been assigned as metal-nitrogen stretching frequencies. Since metal-oxygen-(Lig) vibration will have the same order of frequency as the metal-nitrogen vibrations, it can be suggested that the metal-O-(Lig) vibration will occur at the same region. It is reasonable to assign the 330 cm^{-1} and $490\text{--}485\text{ cm}^{-1}$ to the

V-O (Lig) vibration. This vibration is different from the V-O vibration of the vandyl ion, as the latter is bound by a double bond. So it shows its absorption band at a high frequency.

B. Infrared absorption of a mixture of 2.5% VDEHPA and 0.2 molar pyridines

As pointed out earlier that the primary purpose of this investigation is the finding of the possibility that some pyridines might act as a synergistic agent in the extraction of VO^{2+} by VDEHPA, it becomes necessary to investigate the possibility of interaction between VDEHPA complex and the pyridines. It is pointed out earlier that synergism can only occur if there is an adduct formation between the extracted complex and the pyridines.

Fig. 13-18 represent the spectra obtained with an equilibrium mixture of 2.5 percent VDEHPA and 0.2 molar pyridines. The samples were run against 0.2 molar solution of the same pyridine in the same solvent as indicated in the Figures to cancel out the absorption of pyridines alone. The resulting spectrum shows only the absorption due to VDEHPA and spectrum due to any new absorption which arises because of any interaction. In these experiments some of the other pyridines were also used though they were not used in solvent extraction study. The spectrum obtained was compared with VDEHPA spectrum alone.

The feature which is most striking is that the frequencies of the greater part of the spectrum are unchanged, although there is still a relatively small shift in the spectrum. The general form of the spectrum is also retained. The absorption frequencies of the spectrum are indicated in Table XXXVI. It becomes apparent that P=O vibration is unaltered in the mixture. As seen, the V=O vibration and also V-O-P vibration (as it is supposed to be) are unaltered.

New absorption frequencies are noticed at 1675 and at 1615 for 4BP, at 1620 cm^{-1} for 4EP, at 1615 cm^{-1} for 4lPP, and at 1622 cm^{-1} for beta-Collidine. No new absorption is noticed for 2EP or 2BP. 2EP was not used in the solvent extraction study. The appearance of new bands for 4EP, 4BP, 4lPP and beta-Collidine strongly suggests the formation of new vibrational frequencies for these pyridines. It was pointed out earlier that when strong complexes are formed there is a marked change in the absorption frequencies. The formation of new absorption frequencies in the mixture of VDEHPA and 4-substituted pyridines points to the fact that there is an appreciable change in one of the frequencies of the pyridine nucleus. For 4-substituted pyridines the ring stretching vibrations, which are very near the observed new frequency has the frequency of $1603 \pm 5 \text{ cm}^{-1}$, although the six membered rings show four bands around 1605, 1575, 1480 and 1430 cm^{-1} .

It can be assumed that only the $1605 \pm 5 \text{ cm}^{-1}$ band is strongly affected by the complex formation with VDEHPA in the case of 4EP, 4lPP, and beta-Collidine. In the case of 4BP the same is true, but there is the formation of a new band at 1675 cm^{-1} which is difficult to explain, even if there is no doubt that it has its origin in complexation. That our expectation is right was verified by comparing the spectrum of the above mentioned pyridines themselves with the spectrum of VDEHPA + 4-substituted pyridines (Fig. 19 to Fig. 23). It is found that near the absorption frequencies of about 1600 an absorption peak, or shoulder is found which has a frequency 15-20 cm^{-1} higher in the case of 4-substituted pyridines. No absorption peak is observed for 2-substituted pyridines. As complexation can occur only through the N-atom of pyridines, the increase of stretching frequency indicates that nitrogen is bonded not only to the ring but also to the complex VDEHPA. It seems that 2-substituted pyridines experience steric hindrance to form any complex compound (adduct with the VDEHPA). It has been pointed out that 2-substituted pyridines form much weaker adducts than 4-substituted pyridines with Cu(II) acetyl acetonate. The discovery of no shift in the stretching frequencies of 2-substituted pyridines in mixture with VDEHPA, conforms with Graddon and Watton's²¹ experimental evidence from equilibrium constant data.

The question of attachment of the nitrogen atom undoubtedly involves the state of the vanadyl ion as a whole in the complex VDEHPA. The similarity of the spectrum of the mixture with VDEHPA itself suggest the following:

1. That P=O is bonded as before in the original chelate, as there is no shift of the band to higher frequencies. The ring structure in the chelate is closed. The opening of these ring structures would have caused absorption at a much higher frequency. The intensity of the bands at 1210 and 1235 cm^{-1} would have also been drastically decreased.
2. There is practically no shift or change in intensity in the V-O-[-P] vibration. We have assigned the absorption at 330 cm^{-1} and at 490-495 cm^{-1} to the V-O-[-P] vibration. If two of these bands were destroyed due to complexation, the intensities of these bands would have been drastically changed with new absorption bands appearing in the same region, but at different frequencies. This lack of change indicates that none of the V-O-[-P] bonds are open; the structure remains intact.

It is also noteworthy that the frequency of 930 cm^{-1} attributed to V=O double bond vibration is affected very little by the complexation. Selbin⁶⁷ has noted that the V=O vibration is not appreciably shifted if the molecular weight of the ligand is in excess of 40.

Since the molecular weights of all the pyridines are much greater than 40, Selbin's expectations seem to be fulfilled in this case. Selbin did not point out if his expectations are always true. It will be pointed out later that the contrary might also be true.

C. Infrared spectra of VDEHPA in solution in pyridines

The infrared absorption study was extended to the study of the VDEHPA in pyridine solutions. The object of this study was to find the effect of the solvent on the absorption spectra of VDEHPA. The spectra of VDEHPA in different pyridine solutions are represented in Fig. 24 to 28. Here a 1 percent solution of VDEHPA was compared with a 1 percent solution of VDEHPA in benzene. The same operating conditions were employed as in the determination of the spectrum of VDEHPA in 1 percent benzene solutions.

Fig. 25 shows the spectrum of VDEHPA in 4EP. The spectrum shows P=O stretching bands at 1230 and 1190 cm^{-1} . A band is observed at 1075 cm^{-1} and P-O-C vibration at 1030 cm^{-1} . A shoulder is observed at 950 cm^{-1} and CH_3 wagging vibration at 860 cm^{-1} . In this instance, as before, no shifting of the P=O stretching vibration to higher frequencies occurred. Hence even in a drastic condition where a very large amount of ligand is present as solvent, the chelate ring is resistant to opening. It seems there is a slight shift to the lower frequencies

compared with the absorption frequencies in benzene alone. The decrease in intensity can only be attributed to solvent effect. The appearance of a band at 1075 cm^{-1} can be attributed to solvent effect which displaces the P-O-C stretching vibration to 1030 cm^{-1} unmasking the 1075 cm^{-1} stretching vibration of C-O-[-P]. The C-O vibration seems to be dependent on the pyridine as will be noticed below. The shoulder at 950 cm^{-1} , which has been attributed to V=O vibration, is much more intensified than in the spectra of VDEHPA in benzene alone.

Fig. 24 shows the spectrum of VDEHPA in 2EP. The doublet due to P=O vibration is much widely separated here as the lower frequency band of the doublet is shown at 1160 cm^{-1} . The origin of this separation is difficult to explain as we do not know the origin of the doublet itself. C-O vibration is much more intensified than in 4EP solution and it is more prominent. The band due to V=O vibration is ill developed.

In Fig. 26, which shows the spectrum of VDEHPA in 4BP, the P=O vibration has only one broad band at 1240 cm^{-1} . The C-O vibration of the P-O-C bond is shifted to the higher frequency of 1090 cm^{-1} . P-O-C vibration shows up at 1040 cm^{-1} . V=O vibration shows up again at 950 cm^{-1} and is also greatly intensified.

Fig. 27 represents the spectrum of VDEHPA in 4IPP.

The most interesting thing here is the very weak P=O vibration at 1280 and 1250 cm^{-1} . A broad shoulder is evident around 1150 cm^{-1} . This shoulder can again be attributed to the solvent effect on the vibration P-O bond. The C-O vibration at 1075 cm^{-1} has less intensity in this case. The P-O-C vibration is shifted to a lower frequency. The V=O vibration at 950 cm^{-1} is highly intensified in solution in 4IPP. A peak is observed at 975 cm^{-1} . The origin of this peak may be associated with the V=O vibration.

Fig. 28 represents the spectrum of VDEHPA in beta-Collidine. As in the case of the 4BP solution, the doublet structure of the P-O vibration is replaced by a single vibration at 1240 cm^{-1} . Shown are the C-O vibration at 1080 cm^{-1} , the P-O-C vibration at 1030 cm^{-1} , and the V=O vibration at 950 cm^{-1} .

If the above results are compared with the spectrum of VDEHPA in benzene it seems that the P=O vibration intensity is greatly influenced by the nature of the solvent. The C-O, P-O-C vibration is also shifted to lower, or higher, frequencies according to the pyridine. Although there is a relative shift, it becomes evident that the structure of VDEHPA in solution in pyridine remains practically intact with respect to the bonding of P=O to the central vanadium ion.

The occurrence of a V=O vibration at 950 cm^{-1}

in all pyridines, except 2EP, instead of at 930 cm^{-1} as was found in hexane and benzene solutions, is noteworthy. It seems that solvent effect is responsible for the shift in $V=0$ frequency from 930 cm^{-1} to 950 cm^{-1} .

CHAPTER VIII

UV-VIS AND E.P.R. SPECTRAL STUDY OF VDEHPA

The existence of the VO^{2+} ion was confirmed earlier in the infrared spectral study of the VDEHPA complex. However the approximate structure of the salt is not yet determined. It has been noted elsewhere that the salt has a characteristic blue-green color with waxy consistency. Some idea as to the structure of the complex salt must be formed before the phenomenon of synergism exhibited by the 4-substituted pyridines can be explained. Since definite proof was obtained as to the existence of VO^{2+} group, it was thought that the E.P.R. spectrum of VDEHPA will indicate the approximate structure of VDEHPA. This structure would be found by comparison with salts of the vanadyl ion whose structures have been definitely established. The structure approximated by the E.P.R. spectra can also be further substantiated by the UV-visible spectral study. Before proceeding to discuss the experimental results, it is necessary to represent the information collected about several vanadyl complexes.

Structures of vanadyl ion complexes - Many complexes of vanadyl ion have been prepared. All of them have a characteristic blue or green color. A large number of common bidentate ligands⁷⁵ form 2:1 complexes with VO^{2+} . It seems that only three compounds have been

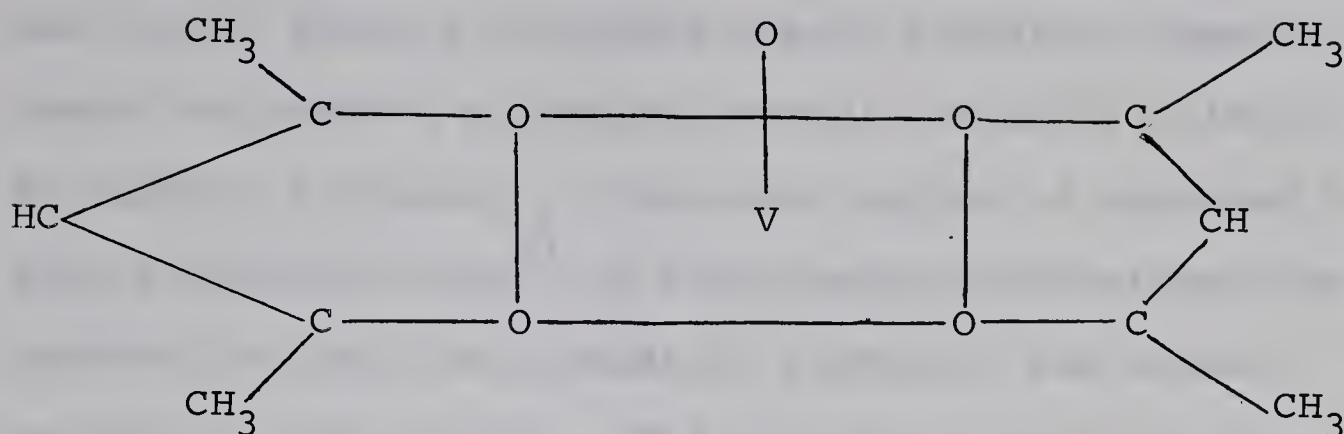
investigated by X-Ray methods. VO_2 was first shown to have a distorted rutile structure in which one V-O bond is much shorter than the others in each VO_6 unit⁷⁶.

The structure of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ is a distorted octahedron which is shown to have VO^{2+} group perpendicular to the base of four water oxygens⁷⁸. The vanadium-oxygen bond length for VO^{2+} is 1.67 Å and the vanadium water oxygen distance is 2.3 Å. The V atom is coplanar with 4 water oxygen atoms. The fifth axial position is occupied by a sulfate group to form a tetragonal structure.

The vanadyl ion in aqueous solution is supposed to also have a tetragonal structure⁷⁹. One oxygen atom is presumed to be nearer to the V atom than the other five surrounding oxygen atoms.

The only vanadyl chelate whose structure is decisively determined is the vanadyl acetyl acetate⁸⁰. The bond distance in the vanadyl ion is 1.56 Å. The five neighbors of vanadium are at the corners of a rectangular pyramid. This configuration is supposed to be formed from the square planar configuration by bending the two chelates away from the fifth oxygen. The four basal V-O distances are approximately 1.97 Å. Each acetyl acetone group was found to be accurately planar, but the two acetyl acetone groups are at an angle of 163°. The fifth axial position is vacant. The structure

of the complex can be represented by:



Paramagnetism of Vanadyl ion - It becomes apparent from the above, that the vanadyl group persists in different compounds and complexes of the vanadyl ion. The vanadyl ion contains a single unpaired d electron. For this reason the vanadyl ion has simple magnetic and spectral properties. The single d electron makes the ion paramagnetic, hence paramagnetic resonance spectra have been noted by several authors for VO^{++} in liquid solutions^{81,82}. The observed spectrum has eight fairly well resolved components corresponding to a nuclear spin of $7/2$. The most interesting feature of the spectrum is the variation of line width with nuclear quantum number m_I .

Because VDEHPA is soluble in suitable organic solvents and is quite stable, the E.P.R. study can be extended to VDEHPA. From the structures of the known vanadyl complexes and from the infrared study, we can assume that VDEHPA has the same structure as vanadyl acetyl acetate, which means that a organophosphorous group takes the place of the acetyl acetate group. The organophosphorous group is expected to be planar

and provide four oxygens to the vanadyl ion. The optical and E.P.R. spectra of VDEHPA should therefore approximate the spectra of vanadyl acetyl acetate. As in $\text{VO}(\text{Acetyl acetate})_2$, the axial oxygen is expected to play a dominant role⁸³ in the interactions between the central ion and the ligands by virtue of its close position to the V atom. The sixth position which is vacant could be occupied by ligands to form 1:1 complexes. The sixth position ligands will affect the axially oriented molecular orbitals. In effect the physico chemical properties of this compound would approximate that of vanadyl acetyl acetate if the compound has the same axial symmetry as that of vanadyl acetyl acetate⁸³.

Molecular Orbital Model of VO^{2+} - The optical spectrum of the vanadyl ion⁸⁴ has been qualitatively explained from the crystal field theory. However the value of the parameter $10 Dq$ postulated from crystal field theory was rather small, while the values of the parameters Ds and Dt are too large. To explain the observed spectra of the vanadyl ion, Ballhausen and Gray⁷⁸, obtained an energy level scheme from a molecular orbital approach. This scheme not only supported the order of energy levels, but also explained a great deal about the spectrum of already known vanadyl complexes. The molecular orbital method was applied to the vanadyl ion in the aqueous phase. To apply this method the assumption was made that the vanadyl ion is co-ordinated with

five molecules of H_2O , with the water oxygen as the donor, out of which four oxygen atoms are co-ordinated on the equatorial square plane and the fifth one co-ordinated on the axial plane. The molecular orbitals were formulated on the experimental result that the $\text{V}=\text{O}$ bond is the strongest bond, and the axial one the weakest. The energy level scheme is depicted in Fig. 53. The figure also explains the various bonding in VO^{2+} in an octahedral environment. The optical and E.P.R. measurements of VDEHPA in different environments should agree with the predictions of Ballhausen and Gray if the complex VDEHPA has the same structure as vanadyl acetyl acetone and VO^{2+} in aqueous solutions.

Experimental

The solution technique was again used to obtain the optical and EPR spectra of VDEHPA in different solvents. The optical spectrum of pure VDEHPA in hexane solution is represented in Fig. 29(a) and 29(b). The spectra was obtained in two parts. The 5% and 2.5% VDEHPA concentration was used for obtaining these spectra. The optical spectrum of VDEHPA in the different pyridine solutions were obtained for the longer wavelengths of the visible spectrum. The UV part of the spectrum could not be obtained in pyridine solutions because of the high absorption of pyridines themselves at shorter wavelengths (around 340 millimicrons). The spectra in

pyridines are represented in Fig. 34-38. To obtain the possible effect of different pyridines on the UV spectrum of VDEHPA, the spectra of a mixture of VDEHPA and pyridines were obtained. It was difficult to go below 300 millimicrons because of strong absorption of pyridines beyond this range. All the absorption spectra were obtained after sufficient time (3-4 hours) was given to obtain complete equilibrium. The spectra were obtained at room temperature (20°C). All spectra of the mixture of VDEHPA and pyridines are represented in Fig. 30-33. The results of the optical measurements are summarised in Table III. The results have been compared with the optical data of other vanadyl complexes and with the data of the vanadyl acetyl acetate chelate. All spectral determinations were repeated several times to ensure reproducibility. The E.P.R. spectrum of VDEHPA in benzene is represented in Fig. 39. The spectra of VDEHPA in different pyridine solutions are represented in Figs. 40-45. In all the cases the spectra were obtained with a Varian 4502 E.P.R. Spectrometer at a constant temperature of 20°C , and at a concentration of 2.5 percent by weight of VDEHPA. Each spectrum was compared with the spectrum of vanadyl acetyl acetate to illustrate the resemblances and differences between the spectrum of VDEHPA with that of vanadyl acetyl acetate. Not all pyridine solutions gave E.P.R. spectra

of good resolution. The hyperfine splitting constants and the spectroscopic splitting factors (g) as determined for the VDEHPA spectra in different pyridine solutions, are given in Tables IV, V and VI for those which gave a workable resolution. The spectra of VDEHPA in 2EP and 2BP did not have resolution. The VDEHPA gave no E.P.R. spectra in 4IPP. Table VII shows the variation of the hyperfine component line width with the nuclear quantum number m_I for VDEHPA in 4BP, 4EP and beta-Collidine.

Another set of E.P.R. spectra of VDEHPA were obtained for the mixture of 2.5 percent VDEHPA and 0.2 molar pyridine in benzene solution. The spectra for these mixtures are given in Fig. 46-48. No attempt was made to calculate the g values from these sets of spectra, but the separation of the individual lines from each other has been indicated in Table VIII. All the determinations were repeated several times. No high temperature E.P.R. study was done. In E.P.R. measurements microwave frequencies of 9.5×10^9 and H_0 values around 3500 oersteds were used.

TABLE III

Solvent Effect on the Optical Spectrum of VDEHPA

	cm^{-1}	cm^{-1}	cm^{-1}
Benzene	13350 (15.2)	15350 (12.8)	-
Hexane	13350 (15.2)	15350 (12.8)	-
4 ethyl pyridine	13350 (24)	17000 (8.5)	29200
4 benzyl pyridine	13350 (35)	17350 (9.7)	Shoulder to the charge transfer spectra*
beta-Collidine	14000 (32.2)	-	30.300
Pyridine	13100 (24)	16200 (8.5)	-

The number in brackets denote extinction coefficient.

*Spectrum obtained in a mixture of VDEHPA and pyridine in benzene solutions.

TABLE IV

Comparison of Optical g Value With E.P.R g Value

	$\langle g \rangle^b$	$\langle A \rangle^b$	g_{II}^a	g_I^a	$\langle g \rangle_a$
Benzene	-	-	1.936	1.983	1.965
Hexane	-	-	1.936	1.983	1.965
4 ethyl pyridine	1.900	107	1.9428	1.983	1.969
4 benzyl pyridine	1.824	111	1.9438	1.9842	1.968
beta-Collidine	1.9433	104	1.9360	1.9842	1.971
Pyridine	1.938	110.1	1.940	1.983	1.968

$\langle A \rangle$ in gaussess,

^aCalculated from optical spectra

^bCalculated from E.P.R. data

TABLE V

Hyperfine Splitting Between Adjacent Lines in Gauss

m_I	1,2	2,3	3,4	4,5	5,6	6,7	7,8	Average $\langle A \rangle$
4-ethyl pyridine	120	95	110	110	110	100	95	- 107
4-benzyl pyridine	110	130	95	145	90	100	-	- 111
beta- Collidine	115	100	105	95	100	100	-	- 104
Pyridine	110	110	110	110	110	115	115	- 110.1

1,2 indicates the splitting between lines 1,2, line one corresponds to $m_I = + 7/2$ and line 8 to $M_I = - 7/2$.

TABLE VI

$\langle g \rangle$ Values Calculated From EPR Data

m_I	7/2	5/2	3/2	1/2	-1/2	-3/2	-5/2	-7/2	Aver- age.
4-ethyl pyridine	1.910	1.910	1.870	1.900	1.910	-	-	-	1.900
beta- Collidine	1.900	1.915	1.930	1.950	1.955	1.970	-	-	1.943
4 benzyl pyridine	1.830	1.820	1.840	1.865	1.800	1.820	-	-	1.938
Pyridine	1.890	1.930	1.943	1.920	1.955	1.960	1.980	-	1.938

TABLE VII

Variation of Line Width in Gausses

With Nuclear Spin Quantum Number m_I

m_I	4 ethyl Pyridine	4 benzyl Pyridine	beta- Collidine	Pyridine
7/2	62.5	-	48	43.12
5/2	33.2	40	33.2	29.44
3/2	25.0	27	25	23.0
1/2	24.0	33.4	24.1	22.95
-1/2	31.7	43.8	31.7	28.84
-3/2	47	46.3	46.8	38.72
-5/2	90	49.3	77.5	62.12
-7/2	-	-	-	87.57

TABLE VIII

The separation of lines in EPR spectrum of a mixture of 0.2 molar pyridines (as noted) and 2.5% VDEHPA in benzene solutions. Splittings in gaussess.

Lines	0.2M 4 ethyl Pyridine	0.2 molar 4 benzyl Pyridine	0.2 molar beta-Collidine
1,2	107.5	100	112.5
2,3	112.5	112.5	112.5
3,4	112.5	115.0	112.5
4,5	112.5	116.0	112.5
5,6	112.5	112.5	112.5
6,7	120	-	115.5
7,8	-	-	112.5
Average	112.9	111.2	112.9

TABLE IX

Spectral data of Vanadyl Complexes (Ballhausen and Gray)

Complex	Medium	Maxima cm ⁻¹	Assignments
VO ²⁺	0.5 - 2M HClO ₄	13100	2B ₂ → 2 E(I)
		16000	2B ₂ → 2 B ₁
		41700	2B ₂ → 2 E(II)
VOSO ₄ ·5H ₂ O	Crystal	13000	2B ₂ → 2 E(I)
		16000	2B ₂ → 2 B ₁
		41700	2B ₂ → 2 E(II)
VO(aca) ₂	C ₂ H ₅ OH	12800	2B ₂ → 2 E(I)
		17300	2B ₂ → 2 B ₁
VO(enta) ₂ ²⁻	H ₂ O	12800	2B ₂ → 2 E(I)
		17200	2B ₂ → 2 B ₁
		29800	2B ₂ → 2 A ₁
VO(oxalate) ₂ ²⁻	H ₂ O	12600	2B ₂ → 2 E(I)
		16500	2B ₂ → 2 B ₁
		29400	2B ₂ → 2 A ₁

Discussion of Optical Spectra

If the assumption is made that the V atom in VDEHPA has almost the same bonding to the four equatorial oxygens as in the hydrated vanadyl ion, and that the vanadium oxygen multiple bond is the same in both cases, then the properties of VDEHPA should depend on the solvent, since the sixth axial position might be vacant, as in the case of $\text{VO}(\text{acac})_2$, and be sterically unhindered. The ion is expected to be strongly perturbed in this direction. Ballhausen and Gray predicted that the perturbation in the axial direction will be manifested in the optical spectrum involving transitions in the $\text{V}=\text{O}$ bond orbital. The g values might also show small changes. According to Ballhausen's model, the first transition will arise due to the moving of the b_2 electron to $e\pi^*$ of the metal orbital, resulting in the $2\text{E}(\text{I})$ excited state. The ground state is 2B_2 in this transition. The energy involved in this transition is about $12,000\text{ cm}^{-1}$ according to the energy level diagram. The first intense band of VDEHPA undoubtedly corresponds to this transition. In $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ the transition has been observed⁷⁸ at 13060 cm^{-1} and the vanadyl acetyl acetone shows the transition⁸³ at $12,800\text{ cm}^{-1}$. For all practical purposes the b_2 level is supposed to be an almost pure 3d_{xy} orbital of vanadium. The $e\pi^*$ orbital is made up of a combination of 3d_{xz} and

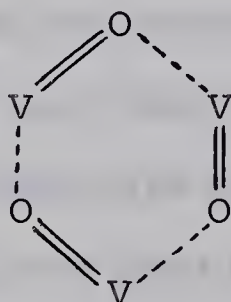
3 d_{yz} orbitals with 2 p_x and 2 p_y oxygen orbitals. Thus any complexation in the axial position is expected to cause changes in the axial compression of V=O bond, resulting in changes in the energy level. Ivan Bernal et al.⁸³ expected that a strong axial perturbation will lower the $e\pi^*$ level with respect to the b_2 level, displacing the absorption band to low energy. As indicated in Table III, their qualitative expectations were not verified by our experiments, but there are small changes of energy involved on changing the solvent from benzene and hexane to pyridine and beta-Collidine. Only in the case of pyridine is the absorption shifted to lower energies by 250 cm^{-1} . In the case of beta-Collidine, the absorption has changed to higher energies with respect to absorption in benzene by about 650 cm^{-1} . The absorption band is not appreciably changed to either a higher or lower energy in 4-ethyl pyridine and 4-benzyl pyridine. Our failure to verify I. Bernal's expectation arises from two sources.

1) All the pyridine derivatives indicated in the table should have almost equal possibility of perturbing the V=O orbital by the lone pair electrons of nitrogen as there is no big substituent group in the ortho position to the nitrogen atom. The small differences that are shown will be due to the differences in electron releasing power of the substituent groups on the pyridine nucleus.

2) The second possibility is that the compound VDEHPA is fundamentally different in some respect from the compound vanadyl acetyl acetonate. Vanadyl acetyl acetonate has been found to be monomeric in benzene solutions⁸³. The $2B_2 \rightarrow 2E(1)$ transition is observed in benzene at $15,150\text{ cm}^{-1}$, which is much higher than the value for $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. Ivan, Bernal et al observed that the absorption band is lowered to $13,020\text{ cm}^{-1}$ in the pyridine solution and to $12,820\text{ cm}^{-1}$ in methanol. In these environments, the absorption frequencies closely approximate the value calculated by Ballhausen and Gray. This is undoubtedly due to the fulfilment of the Ballhausen and Gray postulate that the V atom is hexa coordinated in aqueous and solid phases, as they calculated the energy values on this assumption. Comparison of our optical data with those given in Table IX, strongly suggest that the V(IV) in VDEHPA atom has hexa co-ordinated environment even in benzene and hexane solutions. It was hoped that molecular weight determination of the compound VDEHPA might throw some light on the state of the compound in these solvents. The molecular weight determined by the freezing point depression method gave a value of 1974 in benzene and 1914 in CCl_4 which is almost three times the expected value of 693. Hence the VDEHPA actually exists as a polymer in solutions of non-polar solvents. It is

therefore reasonable to assume that this polymerisation furnishes the axial position the necessary ligand atom to place the central V (IV) atom with octahedral environment. This might be the reason why we do not observe much change of energy of transitions for VDEHPA. As was observed for vanadyl acetyl acetonate; there is no change of octahedral environment of V (IV) in VDEHPA on complexation.

The exact structure of the polymer cannot be ascertained except by X-Ray method. We can however suggest that it might occur through the V=O bond as indicated in the figure below where each oxygen atom of the vanadyl ion forms a loose bond with another vanadium atom to form a six membered strain free cyclic structure.



The assumption of cyclic structure explains the inability of neutral organophosphorous compound to show synergism when they are used in conjunction with di-2-ethyl hexyl phosphoric acid as extractant. This is possibly due to the stronger bond formation with the vanadium atom by the vanadyl oxygen than with the oxygen atom of P=O bond in the neutral organophosphorous compound. The 4-substituted pyridines simply destroy the stable cyclic

structure due to the higher affinity of nitrogen of pyridine for the central vanadium atom. Since the hexa co-ordination of central vanadium is unchanged, the $2B_2 \rightarrow 2E(1)$ transition energy is not significantly changed.

The second transition arises due to the transition from b_2 to b_1^* level, which is composed of a linear combination of the $3d_{x^2-y^2}$ metal orbital and ligand orbitals in the equatorial plane. It is expected that axially directed solvent perturbation will affect this transition only indirectly. It is found from Table III, that in pyridines the transition energy is shifted to higher energy on changing the solvent from benzene to pyridine. This shift occurs probably due to a second-order effect arising out of axial perturbation.

In the UV region the absorption spectra due to the transition $2B_2$ to $2A_1$ are observable in 4-ethyl pyridine and beta-Collidine. They are observable in a mixture of VDEHPA and one of the two pyridines in benzene solutions. Pure pyridines could not be used because of high absorption of the pyridines. These transitions are not at all observable in pyridine, benzene and hexane solutions. Since the transition involves the ground level orbital b_2 to the excited state I_a^* , a high energy change is involved. The transition has been found at $30,000 \text{ cm}^{-1}$ in $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. The values for 4-ethyl pyridine and beta-Collidine is reported in Table III. The values

undoubtedly correspond to the $2B_2 \rightarrow 2A_1$ transition. Since the transition is related to I_a^* which involves a mixture of the metal $3d_{z^2}$ orbital with the metal $4s$ and ligand orbitals, one might expect a shift of the band position with the changes in the solvent. It seems that in VDEHPA, the band is hidden under the first charge transfer band. The complexation with 4-pyridines simply displaces the band to lower energies. A distinct band is shown in 4 ethyl pyridine, and a more or less well developed shoulder is seen with beta-Collidine and 4 benzyl pyridine. The nature of this shift is not clear. The only effect that 4-isopropyl pyridine seems to have on the optical spectra is the complete disappearance of the bands at about $13,000$ and $16,000\text{ cm}^{-1}$ and the intensification and displacement of the charge transfer band to lower energies. The reason for the red shift of the $2B_2 \rightarrow 2A_1$ transition and the charge transfer transition is also not clear. The main reason for the shift may be the formation of complexes which indirectly affect these transitions.

Discussion of the E.P.R. Spectra of VDEHPA - The E.P.R. spectrum of VDEHPA is given in Fig. 39. The E.P.R. spectrum of VDEHPA has been compared with the spectra of vanadyl acetyl acetate. It is seen that VDEHPA shows a broad hump. The spectra of VDEHPA in solvents 4 ethyl pyridine, 4 benzyl pyridine and beta-Collidine

are shown in Figures 43, 44 and 45 respectively. The spectra in the 4-substituted pyridines are resolved to distinct peaks. Only in beta-Collidine are the 8 peaks corresponding to $I = 7/2$ discernable. In other cases, not all the peaks are discernable due to overlapping of the tails of adjacent lines. The effect of simple pyridine has also been represented in Fig. 42. The two substituted pyridines, 2 benzyl pyridine and 2 ethyl pyridine, do not change the E.P.R. spectra of VDEHPA. The only possible explanation for the observed spectra that can be given is that the 4-substituted pyridines and the simple pyridine all form complexes with the VDEHPA. According to a simplified theory presented by McConnell⁸⁸, the observation of a hyperfine structure depends strongly upon complex formation, the applied magnetic field, liquid viscosity, and temperature. To show that only the complex formation is responsible for the observance of hyperfine structure, the E.P.R. spectra were obtained for a mixture of 2.5 percent VDEHPA and 0.2 substituted pyridines in benzene solution. It was seen that 4-substituted pyridines again showed hyperfine structure with the VDEHPA, but the 2-substituted pyridines, 2BP and 2EP, did not show any hyperfine structure. As the same temperature and almost the same magnetic field were used in both cases, it seems only complex formation and viscosity should have the effect on VDEHPA

to show the hyperfine structure. If the viscosity of the 0.2 molar pyridine solutions are supposed to be almost the same in benzene solutions, the inability of 2-substituted pyridines to show hyperfine E.P.R. spectra of vanadyl ion should be attributed to the inability to form complexes with the VDEHPA molecules due to steric effects of 2-substituted groups. Even a small group, like ethyl, is able to hinder the complexation²¹. Spin orbit admixture of the first two excited states with the ground state is expected to give rise to g value anisotropy.

Ballhausen and Gray give the following formula for the calculation of spectroscopic splitting factors g_I and g_{II}

$$g_I = 2 \left[1 - \frac{(C_1^*)^2 \xi}{-E [2B_2 \rightarrow 2E_1]} \right]$$

$$g_{II} = 2 \left[1 - \frac{(C_1^*)^2 4 \xi}{E [2B_2 \rightarrow 2B_1]} \right]$$

where C_1^* values are 0.907 and 0.946 for the first and second excited state according to Ballhausen's calculation. ξ is the spin orbit coupling parameter which is taken as 135 cm^{-1} . The formulas were used to calculate the average $\langle g \rangle$ values from the optical data, from the parallel and perpendicular components of the g tensor,

using the relation $\langle g \rangle = 1/3 (g_{II} + 2g_I)$. The $\langle g \rangle$ values calculated from the optical data for all the solvents are tabulated in Table IV. The g values calculated from the optical data show excellent agreement with the $\langle g \rangle$ values quoted by Rogers and G.E. Pake⁸⁵; B.M. Kozyrev⁸⁶, and others^{83,81}. The calculated values also agree very well with that given for vanadyl acetyl acetone in different solvents⁸³. Hence the $\langle g \rangle$ value shows that the VDEHPA in different solvents have the same electronic structure which is similar to the electronic structure of vanadyl acetyl acetone or $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. The $\langle g \rangle$ values calculated did not show the effect of the solvent as was expected from the optical data.

It was hoped that the $\langle g \rangle$ values calculated from the optical data could be obtained from E.P.R. data with the relation for the paramagnetic resonance

$$\frac{h}{2\pi} \cdot w = \langle g \rangle \beta B_0 + \langle A \rangle m_I$$

where w = microwave frequency, β = Bohr magneton, B_0 = applied magnetic field, $\langle A \rangle$ = the average splitting factor of the VDEHPA in different solutions and m_I = nuclear spin quantum number. (See Appendix for complete theory). The hyperfine splitting constants are reported in Table V. The average hyperfine splitting constant was used for the calculation. The calculated

values are given in Table VI and Table IV. The tables do not show the value for VDEHPA itself because of non-resolution of the hyperfine structure.

It is found that $\langle g \rangle$ values calculated from the E.P.R. data are lower than those calculated from the optical data. Since the optical $\langle g \rangle$ values do not show large deviations, it seems that the calculated values from E.P.R. measurements are affected due to the variation of hyperfine splitting constants from line to line as shown in Table V. Only pyridine gives a reasonable, good agreement with the optical data. Nonetheless, all the values for the different solvents are near the value of 1.9, which shows that the E.P.R. measurement also supports the contention that basically the VDEHPA has the same electronic structure as $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, or other vanadyl complexes.

The hyperfine spacings, $\langle A \rangle$, of VDEHPA in different pyridine solvents are reported in Table V. Table VIII gives the hyperfine spacing of a mixture of 0.2 molar pyridines with 2.5 percent VDEHPA in benzene solutions. In pure solvents there is considerable variation of hyperfine spacing, not only from one solvent to another, but also from one peak to another. In 0.2 molar pyridine solution in benzene, the lines are almost equally separated from each other, the variations between individual lines are much less. The average is listed

for the lines that can be discerned. Hence the averages may not represent the true hyperfine spacing for all the solvents. The changes in hyperfine spacing is of considerable interest to the chemists. I. Bernal et al⁸³ have tried to explain the solvent effect on the vanadyl spectrum on the model of Ballhausen and Gray, the unpaired electron is assumed to be in an almost pure vanadium non-bonding $3d_{xy}$ orbital. The orbitals e_{π}^* and b_I^* have no contribution from the metal S orbital and so cannot contribute to the nuclear hyperfine interaction. I. Bernal⁸³ also thought that the third excited state, I_{aI}^* , has some 4S character, but its high energy level makes little of it available for hyperfine interaction. From the above consideration, Bernal et al postulated that variation in hyperfine splitting from solvent to solvent could arise from the polarisation of filled orbitals like $II a_1^b$ which is expected to have some 4S character and to be strongly influenced by axial perturbation. This could explain the changes in hyperfine interaction. As a matter of fact, no quantitative explanation for this phenomenon is available. Rogers and Pake⁸⁵ qualitatively explained hyperfine spacing on the assumption that the changes in solvents causes a change in the structure of microcrystallite about the central V atom, thereby perturbing the electronic wave function and hence the hyperfine interaction.

No explanation is available for the wide variation

of splitting between individual lines of VDEHPA in different solvents. The average values of the hyperfine splitting constant agrees qualitatively well with the value given for vanadyl acetyl acetonate, in different solvents. Bernal's⁸³ value ranged from 102.3 to 108 gauss. In aqueous⁸⁵ solution, VO^{2+} gives 116 to 118.

Most of the workers have noted a marked variation of line width with the nuclear spin quantum number m_I . The data also shows the variation in line width with nuclear spin quantum number for VDEHPA (Table VII). The experimental line widths were calculated by the method of R. N. Rogers and G. E. Pake⁸⁵. The width of one of the component lines was measured directly, then the width of remaining lines were calculated from their derivative heights from the relation: (derivative height) \times (derivative width)² = constant. The lines were supposed to be of equal intensities. The variation of line width has been studied theoretically by McConnel⁸⁷, and Kivelson⁸⁸. According to McConnel's simplified calculation, the line width is given by $\frac{1}{T_1}$ and $\frac{1}{T_2}$, where T_1 is the spin-lattice relaxation time and T_2 is the transverse relaxation time. The spin lattice relaxation time and the transverse relaxation time both contribute to the broadening of electron paramagnetic resonance lines. McConnel⁸⁷ proposed that total line width $\frac{1}{T_2}$

is given by

$$\frac{1}{T_2} \sim \frac{1}{T_2'} + \frac{1}{T_1}$$

According to McConnell's theory, line width in C.P.S. are given by

$$\frac{1}{T_1} \sim \frac{8\pi^2}{15} (\Delta g \beta H_O + b m_I)^2 h^{-2} T_C / (1 + 4\pi^2 V_O^2 T_C^2)$$

$$\frac{1}{T_2} \sim \frac{32\pi}{45} (\Delta g \beta H_O + b m_I)^2 h^{-2} \tan^{-1}(2T_C/T_2)$$

where $\Delta g = g_{II} - g_I$, $b = A_{II} - A_I$, and H_O is the applied magnetic field.

The above two equations clearly show that line width is dependent on m_I , the nuclear spin quantum number.

From the data in Table VII, it is seen that the sharpest line corresponds to $m_I = 3/2$ in the 4 benzyl pyridine solution. VDEHPA has the sharpest lines for $m_I = 1/2$ in 4 ethyl pyridine, beta-Collidine and pyridine solutions. Since the optical $\langle g \rangle$ values do not show a large shift in $\langle g \rangle$ values as in the case of vanadyl acetyl acetone, it is reasonable to assume that there are wide variations in b for different solvents, i.e. there is wide variations in nuclear hyperfine interactions. The line width variation should also depend on the variations in the rate of tumbling in different solvents, which depend on the effective size of the molecule and the viscosity of the solutions. As a matter of fact T_C , the correlation time, in the above equation takes into

account both the effect of molecular size and the viscosity of the medium, through the relation:

$$T_c = 4\pi n a^3 / 3kT$$

where n is the viscosity of medium, and a is the effective radius of the molecule. Since the effective size of VDEHPA is expected to be much larger than vanadyl acetyl acetate, the lines are expected to be much broader for VDEHPA in solvents than for vanadyl acetyl acetate. This can partly explain the much broader line observed for VDEHPA than for vanadyl acetyl acetate in the same solvents, as can be seen from the figures.

It can be seen that all the E.P.R. data and observed facts indicate that V has almost the same electronic structure in VDEHPA as it has in the vanadyl acetyl acetate and other complexes, except that the VDEHPA is polymerised in non-polar solutions.

CHAPTER IX

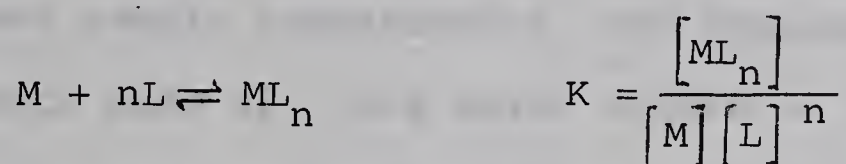
DETERMINATION OF FORMATION CONSTANT AND COMPOSITION OF

ADDUCT BETWEEN 4-PYRIDINES AND $(\text{VDEHPA})_3$

In the foregoing chapters it was established that there is a complexation reaction between the $(\text{VDEHPA})_3$ polymer and the 4-substituted pyridines. It was reasonable to assume that this complexation reaction will be observed as the appearance or shift of band positions in the optical region of the spectra. It was stated earlier that in the UV region, the expected vanadyl vibration near $35,000 \text{ cm}^{-1}$ is masked in the first charge transfer spectra of vanadyl ion. In Fig. 30 and 31, it is shown that a new band appears when VDEHPA reacts with 4-ethyl pyridine and beta-Collidine. It is also shown in Fig. 32, that a shoulder also appears when VDEHPA is reacted with 4BP. As was pointed out earlier this band is the expected VO^{2+} vibration at $35,000 \text{ cm}^{-1}$ which has been shifted to lower frequencies. It is also seen from the figures that intensities of these bands increase with the concentration of pyridine used. In the case of 4IPP there is no indication of a new band, but it seems that the charge transfer band is intensified and is shifted to lower frequencies. Although we could not determine the peak because of strong absorptions of the pyridines at higher frequencies, it was thought that these

new bands could be used to test the composition of the adduct between VDEHPA and pyridines. Such determinations were only made for 4EP and beta-Collidine, as with these pyridines only there is distinct formation of new bands.

Determination of Composition by Variation Method: - The method of continuous variation depends on the use of any additive property provided that this property has different values for each species in the reaction



where M is the metal ion species, L the ligand, K is the formation constant of ML_n . The ratio $\frac{[L]}{[M]} = n$ is satisfied at the maximum concentration of the complex compound ML_n . Hence at maximum $\frac{d[ML_n]}{d[M]} = 0$

So the plot of the absorbance vs composition of the solution will have zero slope at the composition of the complex formed, if the ligands and metal ion species does not absorb in the same range of wave length where the complex absorbs. If the ligand and metal species shows some absorption the line joining the absorbances of 100 percent metal species solution and 100 percent ligand solution alone will indicate the theoretical absorbances of the mixtures of metal ion and ligand species. The absorbances of the complex in the solution is given by the difference of the observed absorbances

at the composition of the mixture. The assumption is made that the complex obeys Beer's Law over the whole concentration range used.

Experimental

The Perkin-Elmer 350 UV-visible spectrophotometer was set for the UV range in the transmittance mode. All the measurements were made at wavelengths as indicated in the Tables XXI and XXII. One cm cells were used in the double beam mode. The solvent, both in reference and sample compartments, was benzene. Stock solutions were made of 0.064 molar VDEHPA on the basis of monomer molecular weight and 0.064 molar solutions of 4-ethyl pyridine and beta-Collidine in benzene. The solutions were prepared as indicated in the Tables by mixing 0, 1, 2, 3, --- 10 ml of VDEHPA to 10, 9, 8, 7, --- 0 ml of pyridine solution in 10 ml volumetric flasks. The solutions after mixing were allowed to stand for 3 hours before the measurements. The data for the measurements are represented in the tables. The data were plotted in Fig. 49 and 50 after correction for the absorption of VDEHPA and pyridine.

Discussion of Composition Data

Figures 49 and 50 indicate that the absorbance of the equimolecular solution of VDEHPA and 4-ethyl pyridine or beta-Collidine reach a maximum near at

50 mol percent VDEHPA and 50 mol percent beta-Collidine. After reaching the maximum the absorbance rapidly fall. It seems that our initial assumption for the validity of the Beer's Law throughout the whole range of compositions is not valid. 4-ethyl pyridine solutions obeys Beer's Law possibly up to 60 percent composition by VDEHPA, after that there is deviation. With beta-Collidine as ligand, the percent VDEHPA vs absorbance plot is also not a straight line. However, the presence of a maximum in both the cases at about 50 percent composition strongly suggests that indeed a 1:1 complex should be involved which is in agreement with the finding for Cu (II) - acetyl acetonate²¹ and for vanadyl acetyl acetonate⁸⁹. Since the complexes could not be isolated from the organic solutions for any of the pyridines studied, only the spectrophotometric data is available. It is presumed that 1:1 complex is also formed for 4BP and 4-isopropyl pyridine for which the composition could not be determined from the spectrophotometric study for the absence of well defined shoulder to the charge transfer spectra. The reason for the failure of Beer's Law after 50 percent composition is not clear, but it might be due to the failure of lower concentrations of pyridines to break up the VDEHPA polymer to monomer for the adduct formation.

Equilibrium Constant Data - On the assumption that 4-pyridines form a 1:1 adduct with VDEHPA, attempts were

made to determine the equilibrium constants for the adduct formation reaction in different solvents. The experimental details have been given elsewhere. The condensed results are given in Table X below and in Tables XXIII to XXXV.

TABLE X

Formation Constant K for the Reaction

$\text{VDEHPA} + \text{B} \rightleftharpoons \text{VDEHPA} \cdot \text{B}$, where B = 4-Pyridines

K in l mol^{-1}

Solvents	4EP	beta-Collidine	4BP	4lPP
Benzene	4.01 ± 1.67	4.96 ± 1.88	1.89 ± 0.54	3.66 ± 0.97
Hexane	1.615 ± 0.31	2.36 ± 0.45	3.85 ± 0.62	-
Chloroform	2.27 ± 0.87	4.75 ± 1.82	3.63 ± 1.53	2.22 ± 0.77

As the results showed the variation of K values, the data in Table X indicates the range of K values that were obtained in at least 15 determinations of K values for each pyridine in each solvent. It is found from Table XXIII to XXXV that with higher concentration of the pyridines, the formation constant of the adduct was approximately constant, but with the use of lower concentrations of pyridine the measured formation constant generally decreases. The decrease of the measured equilibrium constant with decrease of pyridine concentration may be due to the fact that at lower concentrations,

the pyridines have difficulty in forming the complex by breaking up the polymer-- $(\text{VDEHPA})_3$.

It is seen from the data that in hexane and chloroform solutions the equilibrium constant is smaller for 4-ethyl pyridine than for benzene. 4-isopropyl pyridine also seems to show the same behavior, though the equilibrium constant could not be determined in hexane because of the insolubility of 4-isopropyl pyridine in hexane. On the contrary 4BP show higher formation constants in CHCl_3 and hexane. Beta-Collidine has the highest formation constant in benzene and lowest in hexane. There seems to be no order for the abilities of different pyridines as to the adduct formation. It seems that solvation energy, entropy factors and dielectric constant effects of solvents all act differently on different adducts and reactants.

Since in the solvent extraction study kerosine was used as the diluent and there is always an excess of DEHPA in the organic phase, such variations of equilibrium constant is also expected in the kerosine phase, which will be reflected in their synergistic action. Fig. 11 shows the relative effectiveness of the different pyridines in synergic action. As the equilibrium constant data in different solvents suggests that these are of the same order of magnitude, it follows that synergistic ability of the pyridines

should also be of the same order, as is evident in Fig. 11.

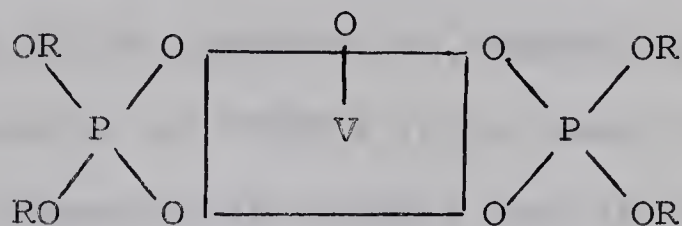
The greater than unity value for the formation (equilibrium) constant suggests the $\text{VDEHPA} \cdot \text{B}$ is more stable than $(\text{VDEHPA})_3$ in the presence of 4-pyridines; the stability of the complex undoubtedly contributes to the increased extraction of V (IV) from the aqueous phase⁶⁶.

CONCLUSION

In the foregoing investigations it becomes clear that the extraction of vanadyl ion by DEHPA proceeds by a simpler mechanism than that shown by the actinides or rare earths, where the extracting acid extracts not only by a liquid ion exchange mechanism but also by solvate formation, which means that the extracting acid itself acts as a solvating agent. Such a mechanism has to be ruled out for VO^{2+} extraction by DEHPA on the grounds of the solvent extraction, molecular weight and compositional data of the extracted species. The solvent extraction data strongly point to the complex formation in the organic phase; molecular weight determinations in benzene and carbon tetrachloride strongly favor the polymerisation of the extracted species in the organic phase.

The infrared spectral study of the organic species VDEHPA, pointed strongly to the presence of a structure where all the significant vibrations could be explained by the formation of a chelate with DEHPA molecules. The infrared study did not show the existence of bonded water molecules with VDEHPA. In confirmation of the solvent extraction data, the infrared study also did not indicate the presence of DEHPA units in the organic species. Hence the solvent extraction reaction could be represented by: $\text{VO}_{\text{aq}}^{2+} + [\text{HX}]_2 \rightleftharpoons \text{VOX}_2 + 2\text{H}^+$

where HX represents DEHPA monomer, and VOX_2 is the monomeric extracted species having the tentative structure



where R is the organic radical. Optical spectra of VDEHPA in benzene and pyridine solvents showed the extracted species has the same octahedral structure for the V (IV) atom as in the vanadyl acetyl acetate. The E.P.R. spectra in 4-pyridines also suggested the same structural environment for V (IV) in VDEHPA.

The IR study also indicated that the 4-substituted pyridines-4-benzyl pyridine, 4-ethyl pyridine and beta-Collidine-give indication of adduct formation with the vanadyl species in the organic phase. This was further confirmed by the E.P.R. spectra which show that VDEHPA has different spectra in inert solvents, such as benzene and hexane, from that in 4-pyridines. E.P.R. spectra also showed that the 2-pyridines -2BP and 2EP- have no effect on the VDEHPA spectra conforming to the fact that IR spectra do not indicate the interaction between 2-pyridines and VDEHPA. Hence the higher extraction by 2BP is difficult to explain as solvent extraction data points to adduct formation.

Although the E.P.R. spectra of VDEHPA in 4-pyridines indicated the existence of an octahedral structure for

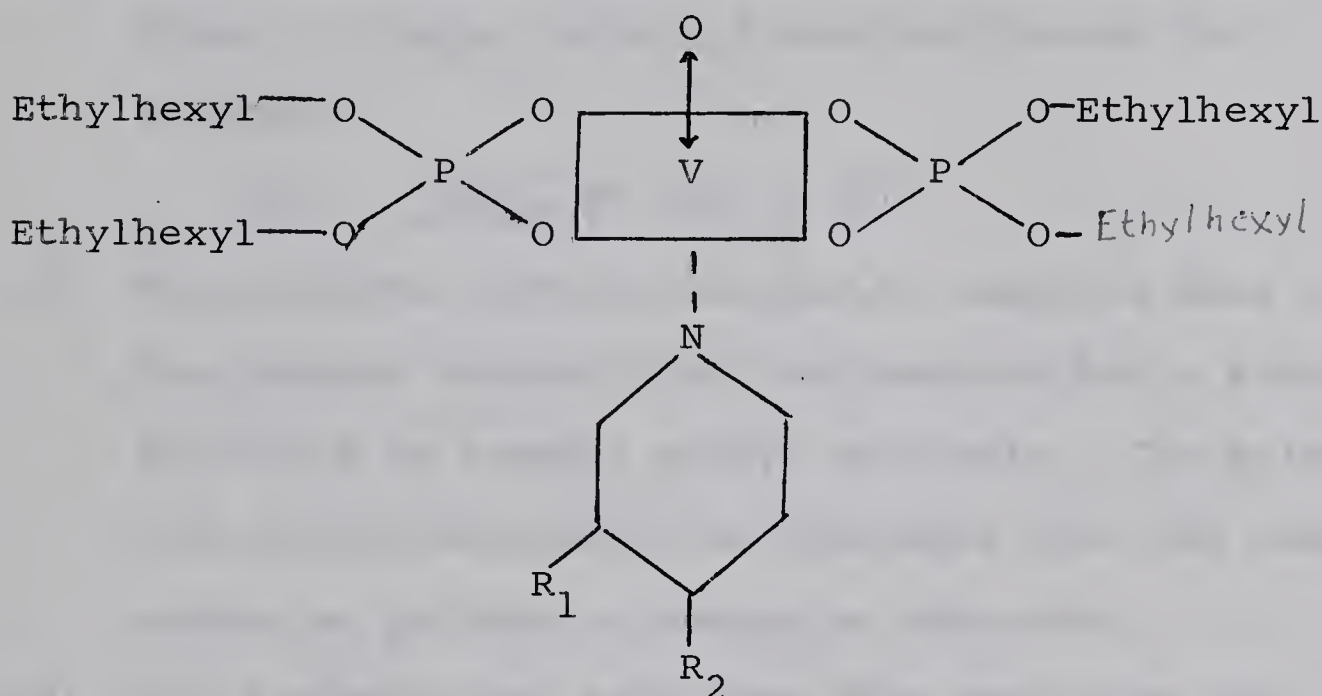
VDEHPA, the spectra of VDEHPA alone in inert solvent benzene is difficult to explain. It is thought that the diffuse E.P.R. spectra of VDEHPA in benzene is due to the existence of VDEHPA in polymeric form, where octahedral symmetry of vanadyl ion is lost to a degree. The existence of tripolymer is indicated by molecular weight determinations in benzene and carbon tetrachloride. It is thought the tripolymer breaks down to a monomer by reaction with pyridines where the condition for showing up the eight lines of E.P.R. spectra of vanadyl ion is favorable.

It seems that the polymerisation of monomeric VDEHPA just after formation is in some way responsible for the inability of DEHPA to further solvate the VDEHPA i.e. VOX_2 . It is suggested that the tripolymer of VDEHPA can arise through the $\text{V}=\text{O}$ double bond to form a ring structure as indicated earlier. A ring structure where vanadyl oxygen acts as a donor can eliminate the basic condition of unsaturation in co-ordination number to show synergistic effects as suggested by Irving and Edgington. This view is in accord with the report in the literature survey that neutral organophosphorous compounds do not show synergism with V (IV). It seems that a much more basic compound like pyridine with a suitable structure can show synergism by breaking up the ring structure. As there is definite indication

of the 1:1 adduct formation, the reaction for synergistic action can take place through the paths

1. $\text{VDEHPA} + 4\text{-Py} \rightleftharpoons \text{VDEHPA} \cdot 4\text{Py}$ 1. immediately after monomer formation
 2. $(\text{VDEHPA})_3 \rightleftharpoons 3 \text{VDEHPA}$ 2. by breaking the polymer forms.
- $\text{VDEHPA} + 4\text{-Py} \rightleftharpoons \text{VDEHPA} \cdot 4\text{Py}$

where $\text{VDEHPA} \cdot 4\text{Py}$ is expected to have the structure

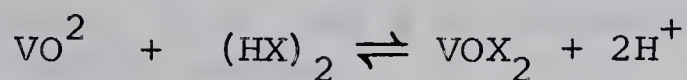


The formation constant of $\text{VDEHPA} \cdot 4\text{Py}$ suggests that $\text{VDEHPA} \cdot 4\text{Py}$ is thermodynamically more stable than $(\text{VDEHPA})_3$ polymer, which it should be for the synergistic complex formation.

SUMMARY OF FINDINGS

(1) The extraction of VO^{2+} by DEHPA is strongly dependent on the anions Cl^- and SCN^- ion in the aqueous phase. The extraction generally decreases with increasing concentrations of Cl^- and SCN^- in the aqueous phase.

(2) DEHPA extracts the vanadyl ion from the aqueous phase by simple chelate formation through the reaction



(3) The infrared, optical and E.P.R. spectral data of the complex suggest that the compound has a similar structure as vanadyl acetyl acetonate. The molecular weight determination indicates that the complex exists as polymer in non-polar solvents.

(4) The 4-substituted pyridines show synergism with the VO^{2+} /DEHPA system, which could be explained by the breaking up of the polymer to form 1:1 complexes of increased stability in the organic phase. The infrared, optical and E.P.R. spectral data indicate the formation of such complexes.

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APPENDIX I

X-Ray Fluorescent Spectroscopy

The principle of X-Ray fluorescent spectroscopy is based upon the fact that secondary fluorescent X-Rays are excited in any substance irradiated with a beam of primary X-Rays and that the spectra of these fluorescent X-Rays is identical in wavelengths and relative intensities when the substance is itself bombarded with electrons in an X-Ray tube. Hence characteristic X-Ray emission spectra of any substance can be obtained by subjecting it to an X-Ray source of sufficient intensity. The intensity of the X-Ray fluorescent beam is dependent on the exciting beam and is very low compared to the exciting beam. Hence a strong X-Ray source is required together with efficient signal amplifying and detecting devices.

Optical System of X-Ray Fluorescent Spectroscopy - The arrangement for the X-Ray fluorescent spectroscopy is shown schematically in the Fig. 51. The main components are X, the primary X-Ray tube, the specimen holder, the collimeter, the analysing crystal, and the detector. The radiations from the X-Ray tube excite secondary characteristic X-Rays of the specimen elements. The specimen may be a solid/solid mixture, or a liquid containing a certain element in solution. As the characteristic X-Rays are emitted in all directions, they are collimated

to a parallel bundle by a collimeter (a parallel array of hollow tubes or blades). Next the parallel beam strikes the analysing crystal. Depending on the position of the crystal only one wave length is diffracted according to the relation

$$n\lambda = 2d \sin \theta$$

where n is the order of diffraction spectra, λ is the wave length in Angstroms, d is the crystal spacing in Å, θ is the angle between the surface of the crystal and the incident radiation after diffraction. The radiation after diffraction is at angle 2θ with respect to the incident beam and its intensity is measured by a detector. To completely cover the whole spectrum, the crystal is rotated from $\theta = 0^\circ$ to $\theta = 90^\circ$, while the detector is automatically turned at twice the speed of the crystal. Since we are interested only in first order spectra, i.e. $n = 1$, θ automatically determines λ at which diffraction occurs and the instrument directly shows the wavelength λ .

Detectors

The intensity of emergent radiation after diffraction is measured by a geiger, proportional or the scintillation counter. The geiger counter combines high efficiency, simple construction, large signal out-put, good stability and very low background. A geiger counter is limited to counting rates of several thousands per second. The proportional counter is able to respond to

high counting rates at a sacrifice in internal gains and so high external pulse amplification is necessary. The scintillation counter combines the high signal output of a geiger counter and the high counting rate of a proportional counter. However the signal to noise ratio is poor compared to that of the geiger counter for soft X-Rays, but much superior for hard X-Rays. The spectral resolution of scintillation counter is inferior to that of proportional counter.

Selection of Crystal Analyser

Many crystals have been tried as analysers though NaCl has been most frequently used, with LiF and Al giving greater intensities. For the elements with atomic number above 21, no complications arise. But with lower atomic weight elements, the absorption by air becomes serious and so a vacuum, or helium, technique has to be used. More caution has to be applied to the choice of the analyser, counter, sample preparation, collimation, and focussing.

Quantitative Analysis by Comparison with Standards

The intensity of the fluorescent beam of a particular wavelength depends on the concentration of the element in the specimen. In general the intensity vs concentration plot for an element in a matrix is not a straight line and hyperbolic plots are common. In making standard curves, it is unnecessary to obtain the whole

curve. Often standards of a few known concentrations are used to get the section of the curve which is pertinent to the analysis. It is necessary to use the same matrix for the element in solid phase or the same solvent in the case of element in solution to avoid the matrix effect.

In the analysis of the raffinate (aqueous) phase from the solvent extraction for vanadium, standard vanadium solutions were prepared from analytical grade ammonium vanadate salt. The intensity vs concentration curve was obtained for the standard V solutions. The concentration in the raffinate could then be obtained directly by noting the intensity in the raffinate solution. The intensity was proportional to counts for a predetermined time. A representative standard curve for V is shown (Fig. 52). Preliminary experiments showed that V could be determined with reproducible results up to approximately 10 mg/litre V. The primary wet methods of analysis were used as a check on the X-Ray method.

Accuracy

As the accuracy of the determination depends on the square root of the total number of counts, precautions were taken to take sufficient number of counts. Theoretically at least 10,000 counts should be taken to reduce the standard deviation below 1 percent.

APPENDIX II

The Theory of Hyperfine Interaction

The interaction of the nuclear spin with electron spin system gives rise to the hyperfine interaction. The hyperfine interaction gives rise to the E.P.R. spectra with the number of lines corresponding to the nuclear spin quantum number I , which can have the discrete values $-I, -I + 1, \dots, I$ in a magnetic field, just as the total spin quantum number S can have values $-S, -S + 1, \dots, S$ in a magnetic field. The interaction of the nuclear spin causes the splitting of energy levels in the spin systems. The energy of the spin system in the presence of magnetic field and hyperfine interaction is calculated from the appropriate Hamiltonian. In the case of a spin system with axial character and $S = 1/2$, the effective spin Hamiltonian is given by

$$H = \beta \left[g_{II} H_r S_r + g_I (H_p S_p + H_q S_q) \right] \text{ Zeeman} \quad (1)$$

$$+ \left[A_{II} I_r S_r + A_I (I_p S_p + I_q S_q) \right] \text{ Hyperfine}$$

The first term in the equation is the Zeeman term, the second one is the Fermi hyperfine interaction term. The p, q, r refers to the axes in the paramagnetic complex. g = g factor, A the hyperfine splitting constant. Transforming to laboratory co-ordinates X, Y, Z , with the Z direction as the direction of magnetic field, The spin Hamiltonian becomes

$$H = \langle g \rangle \beta H_0 S_z + \langle A \rangle I \cdot S. \quad (2)$$

$$\text{where } \langle g \rangle = 1/3 \left[g_{II} + 2 g_I \right]$$

$$\langle A \rangle = 1/3 \left[A_{II} + 2 A_I \right]$$

where II and I denotes the axial values of g and A parallel and perpendicular to the principal axis of the paramagnetic molecule.

In high magnetic fields or small A , the energy levels of the spin system is found from (2) to be corresponding to m_S and m_I as

$$E(m_S, m_I) = \langle g \rangle \beta H_0 m_S + \langle A \rangle m_I m_S \quad (3)$$

Since $[\Delta m_S] = 1$ for transition to occur, we have the corresponding energy difference as $\Delta E = \langle g \rangle \beta H_0 + \langle A \rangle m_I$ (4)

As the m_I can have values $-I$ to $+I$ there are $2I+1$ energy differences, hence there will be $2I+1$ frequencies at which absorption from microwave will occur at a fixed magnetic field. The microwave frequencies are given by

$$\frac{h}{2\pi} \omega = \langle g \rangle \beta H_0 + \langle A \rangle m_I \quad (5)$$

As usually the frequency is kept constant in an E.P.R. spectrometer, there will be $2I+1$ values of H_0 at which there will be resonance lines. The lines are separated from each other by $\langle A \rangle / h$ C.P.S. or $\langle A \rangle / \beta \langle g \rangle$ gauss. The spectroscopic splitting factor $\langle g \rangle$ can be calculated if $\langle A \rangle$ is known from experimental spectra.

TABLE XI

Dependence of Extraction Coefficient of Vanadyl ion on the Concentration of VO^{++} ion in aq. Phase, at Constant pH and DEHPA Concentration.

DEHPA concn. in kerosine	Initial aq. concn. Mol- ar	Aq. concn. after extrac. mg/litre	Concn. in organic mg/litre	Time of extrac.	Initial pH	Final pH	Extrac. coef.	Temp. 20°C
0.03M	0.001	4.0	41.0	10	1.7	1.7	20.3	"
N ¹ series	0.002	5.4	84.6	"	1.7	1.7	15.7	"
	0.003	6.0	129	"	1.7	1.7	21.5	"
	0.004	8.2	172	"	1.7	1.7	20.9	"
	0.005	7.8	217	"	1.7	1.7	27.8	"
	0.006	10.5	295	"	1.7	1.65	28.1	"
	0.007	13.0	302	"	1.7	1.6	23.2	"
	0.008	17.5	342	"	1.7	1.6	19.5	"
	0.009	50	355	"	1.7	1.6	7.0	"
	0.01	20	431	"	1.7	1.6	21.54	"
0.02M	0.001	4.3	40.7	10	1.7	1.6	9.46	"
N ² series	0.002	5.4	89.6	"	1.7	1.7	15.6	"
	0.003	8.0	127	"	1.7	1.6	15.8	"
	0.004	11.0	169	"	1.7	1.6	15.8	"
	0.005	13.5	211	"	1.7	1.65	15.7	"
	0.006	17.5	252	"	1.7	1.65	14.4	"
	0.007	21.2	293	"	1.7	1.65	13.8	"
	0.008	28	332	"	1.7	1.65	11.8	"

TABLE XI (Continued)

DEHPA concn. in kerosine	Initial aq. concn. Mol- ar	Aq. concn. after extrac. mg/litre	Concn. in organic mg/litre	Time of extrac.	Initial pH	Final pH	Extrac. coef.	Temp. 20°C
0.02M N ² series	0.009 0.01	28 30	377 420	10 "	1.7 1.7	1.65 1.65	13.4 14.0	" "
0.01M N ³ series	0.001 0.002 0.003 0.004 0.005 0.006 0.007 0.008 0.009	1.45 3.5 5.25 7.2 10.3 11.0 18.5 21.5 340	43.5 86.5 130 173 215 259 216 338 371	10 " " " " " " " "	2.1 2.1 2.1 2.1 2.1 2.1 2.1 2.1 2.1	2.05 2.05 2.05 2.0 2.0 1.8 1.8 1.8 1.8	30.0 24.7 24.5 24.0 20.8 23.8 16.0 15.7 10.9	" " " " " " " " "
0.04M	0.001 0.002 0.003 0.004 0.005 0.006 0.007	1.47 1.375 1.97 2.6 2.75 3.2 3.6	43.5 88.6. 133 177 222 267 311	10 " " " " " "	2.3 2.3 2.3 2.3 2.3 2.3 2.3	2.25 2.2 2.1 2.1 2.1 2.0 2.0	29.6 64.7 67.5 68.5 81.8 83.4 86.5	" " " " " " "

TABLE XII-A

Dependence of VO^{++} ion Extraction by DEHPA on the
Concentration of HCl ion in the aq. Phase.

DEHPA Concn.	HCl concn. Molar	Initial aq. concn.	Time of extrac. min.	Temp.	Concn. in aq. mg/litre	Concn. in organic mg/litre	Extrac. coef.
0.1 Molar Series 1 A	0.12	0.001	2	20°C	24	21.1	0.879
	0.24	0.001	"	"	36	9.1	0.25
	0.36	0.001	"	"	36	9.1	0.25
	0.48	0.001	"	"	44	1.1	0.025
	0.60	0.001	"	"	40	5.0	0.125
	0.72	0.001	"	"	45	0.0	0.00
	0.84	0.001	"	"	36	9.1	0.25
	0.96	0.001	"	"	40	5.0	0.125
	1.08	0.001	"	"	40	5.0	0.125

TABLE XII-B

Dependence of Extraction Coefficient of VO^{++} by DEHPA on the Chloride ion Concentration in the aq. Phase.

DEHPA concn.	Initial aq. VO^{++} Molar	Chloride ion in aq. phase Molar	Initial pH	Final pH	Temp. 19°C	(min) Time	aq.concn. of VO^{++} after extrac. mg/litre	V concn. in the organic phase mg/litre	Extrac. coef.
0.1 Molar	0.001	0.3	2.6	2.5	19°C	2	1.0	44.1	44.1
	0.001	0.6	2.6	2.4	"	"	1.2	43.9	36.5
Series A^2	0.001	0.9	2.6	2.5	"	"	3.4	41.7	12.2
	0.001	1.2	2.6	2.3	"	"	2.8	92.3	15.1
	0.001	1.5	2.6	2.3	"	"	4.1	41.0	10.0
	0.001	1.8	2.6	2.3	"	"	5.0	40.1	8.0
	0.001	2.1	2.6	2.4	"	"	5.5	39.6	7.2
	0.001	2.4	2.6	2.3	"	"	4.5	40.6	9.0
	0.001	2.7	2.6	2.3	"	"	4.6	40.5	8.8
	0.001	3.0	2.6	2.3	"	"	2.1	43.0	20.4
	0.001	3.5	2.6	2.3	"	"	2.8	42.3	15.1
0.1 Molar	0.001	0.3	3	2.5	19°C	2	2.3	42.8	18.6
	0.001	0.6	"	2.5	"	"	3.4	41.7	12.2
Series A^3	0.001	0.9	"	2.5	"	"	3.7	41.4	11.2
	0.001	1.2	"	2.5	"	"	5.6	39.5	7.05
	0.001	1.5	"	2.5	"	"	4.8	40.3	8.4
	0.001	1.8	"	2.5	"	"	3.6	41.5	11.5
	0.001	2.1	"	2.5	"	"	10.7	34.4	3.21

TABLE XII-B (Continued)

DEHPA concn.	Initial aq. VO ⁺⁺ Molar	Chloride ion in aq. phase Molar	Initial pH		Temp.	(min) Time	aq. concn. of VO ⁺⁺ after extrac. mg/litre	V concn. in the organic phase mg/litre	Extrac. coef.
			pH	Final pH					
0.1 Molar ₃	0.001	2.4	3	2.5	19°C	2	10.7	34.4	3.21
A ₃ Series	0.001	2.7	"	"	"	"	11.0	34.0	3.09
	0.001	3.5	"	"	"	"	15.2	29.9	1.96
	0.001	0.3	4.1	2.7	20°C	2	2.2	42.8	19.4
0.1 Molar ₄	0.001	0.6	4.1	2.7	"	"	1.5	43.5	29.0
	0.001	0.9	4.1	2.7	"	"	3.0	42.0	14.0
	0.001	1.2	4.1	2.7	"	"	4.0	41.0	10.2
A ₄ Series	0.001	1.5	4.1	2.7	"	"	3.5	41.5	11.8
	0.001	1.8	4.1	2.7	"	"	6.0	35.0	5.8
	0.001	2.1	4.1	2.7	"	"	3.0	42.0	14.0
A ₅ Series	0.001	2.4	4.1	2.6	"	"	7.0	38.0	5.4
	0.001	2.7	4.1	2.6	"	"	1.9	43.1	22.6
	0.001	3.0	4.1	2.6	"	"	4.0	41.0	10.2
0.1 Molar ₅	0.01	0.1	1.9	19°C	5	16.0	434	27.0	
A ₅ Series	0.01	0.2	"	"	"	"	15.4	434	28.0
	0.01	0.3	"	"	"	"	10.9	439	40.0
	0.01	0.4	"	"	"	"	10.1	440	43.5
A ₆ Series	0.01	0.5	"	"	"	"	10.3	439	42.6
	0.01	0.6	"	"	"	"	9.1	441	48.6
	0.01	0.7	"	"	"	"	8.2	442	54.0
0.01	0.01	0.8	"	"	"	9.2	441	47.0	

TABLE XIII

Dependence of V(V) Extraction on the Ammonium Thiocyanate
Concentration in the aq. Phase

DEHPA concn. in org. phase		Initial V Thiocya- concn. in aq. phase		Initial	Final	Temp.	Extrac. time min.	Aq. concn. V concn. in	
phase Molar	concn. in aq. phase Molar	pH	pH	mg/litre	after extrac. mg/litre			Extrac. coef.	
0.1 Molar B ¹ Series	0.01	0.1	3.1	1.9	19°C	5	50	401	8.0
	0.01	0.2	3.1	1.9	"	"	64	387	6.04
	0.01	0.3	3.1	2.0	"	"	107	344	3.20
	0.01	0.4	3.1	2.0	"	"	140	311	2.22
	0.01	0.5	3.1	2.0	"	"	157	294	1.87
	0.01	0.6	3.05	2.05	"	"	185	266	1.43
	0.01	0.7	3.05	2.05	"	"	210	241	1.14
	0.01	0.8	3.05	2.1	"	"	227	224	0.985
0.1 Molar B ² Series	0.01	0.1	2.5	1.8	19°C	5	70	380	5.4
	0.01	0.2	2.5	1.9	"	"	109	341	3.13
	0.01	0.3	2.5	1.9	"	"	157	293	1.87
	0.01	0.4	2.5	1.95	"	"	176	275	1.56
	0.01	0.5	2.5	1.95	"	"	195	256	1.31
	0.01	0.6	2.5	2.00	"	"	219	232	1.06
	0.01	0.7	2.5	2.00	"	"	241	210	0.87
	0.01	0.8	2.15	2.00	"	"	260	190	0.73
0.1 Molar B ³ Series	0.01	0.1	4.5	1.9	19°C	5	87	364	4.18
	0.01	0.2	4.5	1.9	"	"	107	344	3.21
	0.01	0.3	4.5	2.0	"	"	155	296	1.91

TABLE XIII (Continued)

DEHPA concn. in phase	Initial V concn. in aq. phase Molar	Thiocyanate concn. Molar	Initial pH	Final pH	Temp. °C	Extrac. time min.	Aq. concn. of V after extrac. mg/litre	V concn. in org. phase after extrac. mg/litre	Extrac. coef.
³ B ₃ series of extractions were done to find if there is any major change of extraction after 24 hours of preparation of the aq. phase.									
0.01	0.01	0.4	4.5	2.0	19°C	5	260	191	.73
0.01	0.01	0.5	4.5	2.0	"	"	199	252	1.26
0.01	0.01	0.6	4.5	2.0	"	"	227	224	0.98
0.01	0.01	0.7	4.5	2.0	"	"	254	197	0.77
0.01	0.01	0.8	4.5	2.0	"	"	254	197	0.77
⁴ B ₄ series									
0.01	0.01	0.01	1.9	1.9	19°C	5	8.5	442	52
0.01	0.01	0.02	1.9	1.9	"	"	14.1	436	30
0.01	0.01	0.03	1.9	1.9	"	"	21.0	429	20.4
0.01	0.01	0.04	1.9	1.9	"	"	21.5	429	19.9
0.01	0.01	0.05	1.9	1.9	"	"	26.9	424	15.7
0.01	0.01	0.06	1.9	1.9	"	"	26.9	424	15.7
0.01	0.01	0.07	1.9	1.9	"	"	25.7	425	16.5
0.01	0.01	0.08	1.9	1.9	"	"	28.5	429	14.9
⁵ B ₅ series									
0.001	0.001	0.1	2.55	2.55	19°C	5	1.0	44	44
0.001	0.001	0.2	2.55	2.55	"	"	1.0	44	44
0.001	0.001	0.3	2.55	2.55	"	"	1.7	43.3	25
0.001	0.001	0.4	2.55	2.55	"	"	3.9	41.1	10
0.001	0.001	0.5	2.55	2.55	"	"	4.1	40.2	9.8
0.001	0.001	0.6	2.55	2.55	"	"	5.3	39.7	7.5
0.001	0.001	0.7	2.55	2.55	"	"	7.2	37.8	5.3
0.001	0.001	0.8	2.55	2.55	"	"	10.0	35.0	3.5

TABLE XIV

Dependence of Extraction of Vanadium (IV) by DEHPA on the NO_3^- ion Concentration in the aq. Phase

DEHPA concn. Molar	Initial Vanadium (IV) concn. in the aq. phase Molar	Anion concn. in the aq. phase Molar	Final pH	Time of extrac. min.	Temp. $^{\circ}\text{C}$	Aq. concn. of Vanadium extrac. mg/litre	Organic Vanadium concn. mg/litre	Extrac. coef.
0.1 Molar	0.01	0.1	1.9	5	19 $^{\circ}\text{C}$	14.4	436	30.3
	0.01	0.2	1.9	"	"	16.2	434	26.8
	0.01	0.3	1.9	"	"	15.4	435	28.3
	0.01	0.4	1.9	"	"	12.6	438	34.8
	0.01	0.5	1.9	"	"	17.4	433	25.0
	0.01	0.6	1.9	"	"	8.6	442	51.4
	0.01	0.7	1.9	"	"	12.0	439	36.5
	0.01	0.8	1.9	"	"	12.5	432	36.5
0.1 Molar	0.01	1.0	1.8	5	21 $^{\circ}\text{C}$	8.0	443	55.3
	0.01	2.0	1.6	"	"	5.0	446	89.2
	0.01	3.0	1.5	"	"	5.1	446	87.1
	0.01	4.0	1.4	"	"	5.0	446	89.1
	0.01	5.0	1.3	"	"	4.7	446	94.9
0.1 Molar	0.001	0.1	2.5	5	21 $^{\circ}\text{C}$	2.1	42.9	20.4
	0.001	0.2	2.5	"	"	1.57	43.4	27.6
	0.001	0.3	2.5	"	"	1.34	43.6	32.5
	0.001	0.4	2.5	"	"	0.94	44.0	46.0
	0.001	0.5	2.5	"	"	1.48	43.5	29.4
	0.001	0.6	2.5	"	"	1.72	43.2	25.4
	0.001	0.7	2.5	"	"	1.54	43.4	28.3
	0.001	0.8	2.45	"	"	1.16	43.8	42.0

TABLE XV

Dependence of the Extraction of V(IV) on the pH of the Aqueous Phase

DEHPA concn.	Initial V concn.	Equili- brium pH	Aq. V concn. mg/l	Organic V concn. mg/l	Time	Extraction coeff.	Log Ex- traction coeff.	Temp.
0.4 Molar	5×10^{-3} Mol.	1.5	16.1	209	5 min.	13.0	1.24	20^{0+2}
		1.7	3.83	221	"	56.0	1.74	"
		1.95	3.07	221	"	71.6	1.85	"
		2.4	1.84	223	"	121	2.08	"
		3.4	1.32	223	"	156	2.19	"
		2.25	1.95	223	"	114	2.05	"
0.05 Molar	5×10^{-3} Mol.	2.52	1.03	224	"	217	2.33	"
		1.6	122	103	5 min.	0.84	1.92	20^{0+2}
		1.8	40.4	185	"	4.6	0.66	"
		2.1	15.3	209	"	13.7	1.13	"
		2.4	7.8	217	"	27.8	1.44	"
0.05 Molar	5×10^{-3} Mol.	3.0	3.4	222	"	66.0	1.81	"

TABLE XVI

Dependence of Extraction on the DEHPA Concentration in the Organic Phase V(IV) Initial Concentration 5×10^{-3} Molar.

<u>V</u> <u>Concn.</u>	<u>Eg.pH</u>	<u>DEHPA</u> <u>Concn.</u> <u>Molar</u>	<u>Aq.</u> <u>Concn.</u> <u>mg/l</u>	<u>Organic</u> <u>Concn.</u> <u>mg/l</u>	<u>Time</u> <u>(min)</u>	<u>Temp.</u>	E_a^O <u>Extrac.</u> <u>Coeff.</u>
5×10^{-3}	1.55	0.40	5.1	177	5	20 ± 2	34.6
		0.30	7.0	174	"	"	25.0
		0.20	15.0	167	"	"	11.1
		0.10	34.5	147	"	"	4.26
		0.05	65.0	117	"	"	1.80
		0.01	153	28.6	"	"	0.186
$5 \times 10^{-3} M$	1.45	0.40	11.4	142	"	"	12.6
		0.30	16.0	138	"	"	8.60
		0.20	34.3	120	"	"	3.49
		0.10	58.0	96.0	"	"	1.65
		0.05	78.2	75.8	"	"	0.969
		0.01	145	19.2	"	"	0.132
$5 \times 10^{-4} M$	2.85	0.40	0.21	19.8	"	"	98.0
		0.10	0.32	19.7	"	"	61.5
		0.05	0.47	19.5	"	"	41.5
		0.01	0.68	19.3	"	"	28.4
		0.005	0.82	19.1	"	"	23.0
		0.001	8.2	11.8	"	"	7.6

TABLE XVII

Dependence of the V(IV) Extraction on the Tri-iso-octyl Concentration
in the Organic Phase DEHPA Concentration 0.1 Molar

T _I OA Concn. Molar	Initial V(IV) Concn.	Eq. pH	Aq. Phase Concn.	Organic Phase Concn.	Time	Temp.	Extraction Coeff.
0.01	901 mg/l	2.3 ⁺ ₋₁	142	759	5 min.	20 ⁺ ₋₂ °C	5.3
0.02	"	"	255	645	"	"	2.52
0.04	"	"	250	381	"	"	0.735
0.06	"	"	729	172	"	"	0.236
0.08	"	"	799	102	"	"	0.128
0.10	"	"	807	94	"	"	0.118
0.01	450 mg/l	2.35	35.6	414	5 min.	20 ⁺ ₋₂ °C	10.6
0.02	"	"	76.0	374	"	"	4.9
0.04	"	"	214	236	"	"	1.1
0.06	"	"	407	43.0	"	"	0.132
0.08	"	"	403	47.0	"	"	0.112
0.10	"	"	402	47.2	"	"	0.119
0.01	250 mg/l	2.2 ⁺ ₋₁	10.9	239	5 min.	20 ⁺ ₋₂ °C	19.7
0.02	"	"	22.5	227	"	"	8.65
0.04	"	"	93.2	157	"	"	1.41
0.06	"	"	182	68.3	"	"	0.237
0.08	"	"	192	58.2	"	"	0.179
0.10	"	"	209	41.0	"	"	-

TABLE XVIII

Dependence of the Extraction of V(IV) from Aqueous Buffers

Initial V(IV) Concentration 0.004 Molar

<u>Eq. pH</u>	<u>DEHPA Concn.</u>	<u>Organic Concn.</u>	<u>Aq. Concn. mg/l V</u>	<u>Time</u>	<u>Temp.</u>	<u>Extrac- tion Coeff.</u>
2.18	0.1 Mol.	142	3.58	1 hr.	20 [±] 2	40
2.23	"	142	3.58	"	"	40
3.42	"	145	0.6	"	"	242
3.89	"	145	1.0	"	"	145
4.12	"	143	1.0	"	"	145
4.32	"	141	2.51	"	"	57.5
4.49	"	95.7	4.90	"	"	28.8
4.66	"	84.4	40.3	"	"	2.2
4.80	"	73.0	51.6	"	"	1.64
2.25	0.01 Mol.	112	34.1	"	"	3.28
2.35	"	121	24.2	"	"	5.00
3.48	"	142	4.0	"	"	35.0
3.92	"	143	3.0	"	"	42.5
4.15	"	141	4.1	"	"	35.2
4.37	"	141	5.0	"	"	28.2
4.53	"	142	3.8	"	"	37.2
4.72	"	138	7.5	"	"	18.2
4.90	"	104	42.5	"	"	2.48
5.16	"	56	90.0	"	"	0.68

TABLE XVIII (Cont'd)

<u>Eq. pH</u>	<u>DEHPA Concn.</u>	<u>Organic Concn.</u>	<u>Aq. Concn. mg/l V</u>	<u>Time</u>	<u>Temp.</u>	<u>Extrac- tion Coeff.</u>
2.76	0.02 Mol.	137	8.7	1 hr.	20±2	16.8
3.43	"	139	8.3	"	"	16.8
3.73	"	143	3.0	"	"	47.7
4.27	"	141	1.0	"	"	141
4.45	"	143	2.4	"	"	59.5
4.63	"	145	1.5	"	"	96.5
4.80	"	137	38.8	"	"	15.8
4.99	"	108	38.0	"	"	2.84
5.23	"	89.2	56.8	"	"	1.60

TABLE XIX

Dependence of the Extraction of V(IV) on the Various Pyridine Derivatives in the Organic Phase, with a Constant H₂SO₄ Concentration in the Aqueous Phase and Constant DEHPA Concentration in the Organic Phase.

Concn. of 4-Ethyl Pyridine	DEHPA Concn.	Initial V concn. g/l	Aq. Concn. mg/l V	Organic Concn. mg/l V	Extrac- tion Coeff.	Time 1 hr.	Temp.	H ₂ SO ₄ Concn.
0.01	0.05 Molar	1.095	471	549	1.17	1 hr.	20±2	5 x 10 ⁻² molar
0.02	"	"	412	608	1.48	"	"	"
0.04	"	"	292	728	2.49	"	"	"
0.06	"	"	180	815	3.98	"	"	"
0.10	"	"	108	840	4.67	"	"	"
0.20	"	"	108	912	8.43	"	"	"
0.30	"	"	71.9	948	13.2	"	"	"
Conc. of 4-isopropyl Pyridine								
0.01	0.05 Molar	1.095	438	582	1.33	"	"	"
0.02	"	"	368	651	1.77	"	"	"
0.04	"	"	222	798	3.60	"	"	"
0.06	"	"	194	826	4.26	"	"	"
0.10	"	"	269	751	2.79	"	"	"
0.20	"	"	399	620	1.55	"	"	"

TABLE XIX (Continued)

Concn. of 2-Benzyl Pyridine	DEHPA Concn.	Initial V concn. g/l	Aq. Concn. mg/l V	Organic Concn. mg/l V	Extrac- tion Coeff.	Time 1 hr.	Temp. 20 ⁺ -2	H ₂ SO ₄ Concn. 5 x 10 ⁻² molar
0.02	0.05 Molar	1.095	402	618	1.53	1	20 ⁺ -2	"
0.04	"	"	272	747	2.74	"	"	"
0.06	"	"	209	810	3.86	"	"	"
0.08	"	"	190	829	4.25	"	"	"
0.10	"	"	179	840	4.69	"	"	"
0.20	"	"	130	889	6.81	"	"	"
Concn. of 2-5 nonyl Pyridine								
0.02	"	"	259	839	3.23	"	"	"
0.04	"	"	233	865	3.71	"	"	"
0.06	"	"	209	889	4.25	"	"	"
0.08	"	"	195	903	4.63	"	"	"
0.10	"	"	173	925	5.34	"	"	"
Concn. of 4-Benzyl Pyridine								
0.01	"	1.072	658	414	0.62	"	"	"
0.02	"	"	610	462	0.76	"	"	"
0.04	"	"	489	583	1.18	"	"	"
0.06	"	"	392	680	1.73	"	"	"
0.08	"	"	279	793	2.70	"	"	"
0.10	"	"	182	890	4.80	"	"	"
0.20	"	"	166	906	5.65	"	"	"

TABLE XX

Dependence of Extraction of V(IV) on the H_2SO_4 Concentration at Constant DEHPA Concentration and at Constant Concentration of Pyridine Derivatives.

	H_2SO_4 Concn. Molar	Aq.phase V concn. mg/l V	Organic phase V concn. mg/l V	Extraction Coeff.	Time	Temp	DEHPA Concn.
With 2 Benzyl Pyridine	0.01	43	1055	24.5	1 hr.	20 [±] 2	0.05 Molar
	0.02	110	988	8.98	"	"	"
0.05 Molar	0.04	302	796	2.63	"	"	"
	0.06	509	589	1.15	"	"	"
	0.10	618	480	0.776	"	"	"
	0.20	695	403	0.579	"	"	"
	0.30	814	284	0.348	"	"	"
With 4- isopropyl Pyridine	0.01	154	986	6.40	"	"	"
	0.02	262	878	3.35	"	"	"
0.05 Molar	0.04	497	643	1.29	"	"	"
	0.06	655	485	0.740	"	"	"
	0.08	819	321	0.391	"	"	"
	0.10	972	168	0.172	"	"	"
	0.20	1140	0	0	"	"	"
With 4 Benzyl Pyridine	0.01	69	1003	14.5	"	"	"
	0.02	149	923	6.20	"	"	"
0.05 Molar	0.04	340	732	2.14	"	"	"
	0.06	532	540	1.01	"	"	"
	0.08	688	384	0.550	"	"	"
	0.10	775	297	0.384	"	"	"
	0.20	810	262	0.324	"	"	"
	0.30	960	112	0.117	"	"	"

TABLE XX (Continued)

	<u>H₂SO₄</u> <u>Concn.</u> <u>Molar</u>	<u>Aq. phase</u> <u>V concn.</u> <u>mg/l V</u>	<u>Organic</u> <u>Phase</u> <u>V concn.</u> <u>mg/l V</u>	<u>Extraction</u> <u>Coeff.</u>	<u>Time</u>	<u>Temp.</u>	<u>DEHPA</u> <u>Concn.</u>
With 2-5 nonyl Pyridine	0.01	271	865	3.19	1 hr.	20 ⁺ 2	0.05 Mol.
	0.02	364	772	2.12	"	"	"
0.05 Molar	0.04	467	669	1.43	"	"	"
	0.06	737	399	0.541	"	"	"
	0.08	834	302	0.362	"	"	"
	0.10	927	209	0.225	"	"	"
With 4-ethyl Pyridine	0.01	32.5	1065	32.7	"	"	"
	0.02	125	973	7.78	"	"	"
0.05 Molar	0.04	345	753	2.18	"	"	"
	0.06	519	579	1.11	"	"	"
	0.08	681	417	.612	"	"	"
	0.10	748	350	.467	"	"	"
	0.20	929	169	.181	"	"	"
DEHPA alone	0.01	300	798	2.66	"	"	"
	0.02	463	635	1.37	"	"	"
	0.04	640	458	.715	"	"	"
	0.06	710	388	.546	"	"	"
	0.08	798	300	.376	"	"	"

TABLE XXI

Spectrophotometric determination of the composition of the adduct between VDEHPA and 4EP.

100% VDEHPA solution 0.064 Molar; 100% 4EP solution 0.064 Molar.

Wave Length milli- microns	mls of 0.064 Mol. VDEHPA in 10 ml.	mls of 0.064 Mol. 4EP in 10 ml.	Transmittances				Aver- age T	Ab- sorbance
			T ₁	T ₂	T ₃	T ₄		
346	0	10	0.910	0.900	0.910	0.900	0.905	0.430
	1	9	0.630	0.630	0.630	0.630	0.630	0.201
	2	8	0.300	0.300	0.310	0.320	0.307	0.512
	3	7	0.215	0.220	0.225	0.230	0.222	0.654
	4	6	0.150	0.155	0.160	0.170	0.158	0.801
	5	5	0.130	0.135	0.135	0.135	0.134	0.873
	6	4	0.180	0.190	0.190	0.195	0.188	0.726
	7	3	0.650	0.650	0.650	0.660	0.652	0.183
	8	2	0.720	0.720	0.725	0.725	0.722	0.141
	9	1	0.720	0.720	0.720	0.725	0.722	0.141
	10	0	0.720	0.720	0.720	0.720	0.720	0.141
330	0	10	0.850	0.860	0.860	0.850	0.855	0.068
	1	9	0.595	0.590	0.595	0.595	0.594	0.226
	2	8	0.260	0.260	0.265	0.265	0.262	0.582
	3	7	0.200	0.200	0.210	0.210	0.205	0.688
	4	6	0.160	0.165	0.165	0.165	0.164	0.785
	5	5	0.145	0.150	0.152	0.160	0.152	0.818
	6	4	0.190	0.190	0.195	0.200	0.168	0.775
	7	3	0.625	0.630	0.630	0.630	0.628	0.201
	8	2	0.665	0.665	0.665	0.670	0.666	0.176
	9	1	0.665	0.670	0.670	0.670	0.668	0.173
	10	0	0.675	0.675	0.675	0.675	0.675	0.172
360	0	10	0.890	0.890	0.890	0.900	0.892	0.050
	1	9	0.660	0.660	0.660	0.660	0.660	0.181
	2	8	0.480	0.510	0.540	0.540	0.540	0.286
	3	7	0.300	0.300	0.310	0.315	0.306	0.514
	4	6	0.220	0.220	0.220	0.225	0.221	0.656
	5	5	0.200	0.200	0.200	0.205	0.201	0.697
	6	4	0.240	0.260	0.265	0.270	0.258	0.588
	7	3	0.665	0.660	0.660	0.665	0.662	0.178
	8	2	0.740	0.740	0.740	0.740	0.740	0.131
	9	1	0.730	0.730	0.730	0.730	0.730	0.137
	10	0	0.720	0.720	0.725	0.725	0.722	0.142

TABLE XXII

Spectrophotometric determination of the composition of the adduct between VDEHPA and beta-Collidine. 100% VDEHPA concentration 0.064 Molar; 100% beta-Collidine concentration 0.064 Mol.

Wave Length milli- microns	mls of 0.064 Mol. VDEHPA in 10 ml.	mls of 0.064 beta-Coll. in 10ml.	Transmittances				Aver- age T	Ab- sorbance
			T ₁	T ₂	T ₃	T ₄		
340	0	10	0.730	0.730	0.730	0.730	0.730	0.131
	1	9	0.290	0.32	0.31	0.31	0.307	0.513
	2	8	0.210	0.210	0.200	0.200	0.205	0.689
	3	7	0.160	0.165	0.160	0.160	0.161	0.793
	4	6	0.130	0.130	0.130	0.135	0.131	0.883
	5	5	0.130	0.130	0.135	0.135	0.132	0.879
	6	4	0.180	0.190	0.195	0.215	0.195	0.710
	7	3	0.625	0.630	0.630	0.630	0.625	0.204
	8	2	0.670	0.670	0.675	0.670	0.670	0.174
	9	1	0.680	0.680	0.680	0.680	0.680	0.168
	10	0	0.685	0.685	0.685	0.685	0.685	0.165
355	0	10	0.78	0.775	0.775	0.775	0.776	0.112
	1	9	0.340	0.345	0.350	0.350	0.346	0.461
	2	8	0.210	0.215	0.215	0.215	0.214	0.670
	3	7	0.170	0.170	0.170	0.165	0.168	0.775
	4	6	0.145	0.140	0.150	0.150	0.146	0.836
	5	5	0.150	0.145	0.150	0.150	0.148	0.830
	6	4	0.230	0.235	0.245	0.250	0.240	0.620
	7	3	0.650	0.650	0.650	0.650	0.650	0.187
	8	2	0.690	0.690	0.690	0.690	0.690	0.161
	9	1	0.700	0.700	0.700	0.700	0.700	0.155
	10	0	0.700	0.700	0.695	0.700	0.695	0.156
370	0	10	0.820	0.820	0.815	0.815	0.812	0.091
	1	9	0.570	0.578	0.585	0.590	0.581	0.237
	2	8	0.390	0.385	0.385	0.385	0.387	0.413
	3	7	0.310	0.300	0.305	0.305	0.305	0.517
	4	6	0.260	0.265	0.265	0.270	0.265	0.575
	5	5	0.270	0.270	0.270	0.270	0.270	0.569
	6	4	0.450	0.460	0.470	0.505	0.471	0.327
	7	3	0.690	0.690	0.690	0.690	0.690	0.161
	8	2	0.720	0.715	0.715	0.715	0.716	0.146
	9	1	0.725	0.720	0.720	0.720	0.721	0.143
	10	0	0.715	0.715	0.715	0.710	0.714	0.147

TABLE XXIII

Spectrophotometric determination of equilibrium constant (K) of the reaction $\text{VDEHPA} + \text{beta-Collidine} \rightleftharpoons [\text{ADDUCT}]$ VDEHPA concentration 7.2 millimolar, equilibration time 3 hr. Temp. 23°C, D = Absorbance, D_c = corrected D, B = Base. Solvent, benzene.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K $l \text{ mol}^{-1}$
			T_1	T_2	T_3				
I	340	160.8	0.02	0.02	0.02	0.02	1.699	1.491	7.2
		120.6	0.045	0.045	0.045	0.045	1.347	1.179	6.2
		100.5	0.075	0.075	0.075	0.075	1.125	1.084	5.1
		80.4	0.12	0.12	0.12	0.12	0.921	0.736	4.8
		40.2	0.44	0.455	0.46	0.448	0.349	0.279	2.6
		20.1	0.68	0.68	0.68	0.168	0.168	0.141	2.58
		8	0.85	0.855	0.855	0.068	0.68	0.063	2.48
II	340	160.8	0.02	0.01	0.01	0.15	1.824	1.616	8.5
		120.6	0.045	0.045	0.045	0.045	1.347	1.179	6.2
		100.5	0.075	0.075	0.08	0.0766	1.114	0.973	5.5
		80.4	0.120	0.120	0.120	0.120	0.921	0.796	4.3
		40.2	0.465	0.470	0.465	0.466	0.351	0.281	2.6
		20.1	0.670	0.670	0.675	0.672	0.171	0.144	2.5
		8	0.83	0.83	0.83	0.830	0.081	0.076	3.34
III	340	164.8	0.025	0.025	0.025	0.025	1.602	1.394	6.1
		120.6	0.065	0.065	0.065	0.065	1.187	1.019	4.76
		100.5	0.09	0.09	0.09	0.09	1.046	0.905	4.5
		80.4	0.140	0.140	0.140	0.140	0.854	0.629	3.45
		40.2	0.515	0.525	0.53	0.520	0.188	0.118	1.17
		20.1	0.68	0.69	0.69	0.688	0.166	0.139	2.46
		8	0.85	0.84	0.845	0.845	0.074	0.069	3.24
IV	340	164.8	0.02	0.02	0.02	0.02	1.699	1.491	7.0
		120.6	0.045	0.045	0.045	0.045	1.347	1.179	5.95
		100.5	0.065	0.065	0.065	0.065	1.187	1.046	5.65
		80.4	0.11	0.11	0.115	0.112	0.951	0.826	5.2
		40.2	0.425	0.435	0.44	0.426	0.247	0.177	2.56
		20.1	0.67	0.675	0.675	0.673	0.172	0.145	2.54
		8	0.84	0.85	0.85	0.846	0.073	0.68	3.23

TABLE XXIV

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{IPP} \rightleftharpoons [\text{ADDUCT}]$ in benzene VDEHPA concentration 7.2 millimolar, equilibration time 3 hr. Temp. 23°C, D= Absorbance, D_c =Corrected D, B=Base. K, l mol^{-1} .

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K
			T_1	T_2	T_3				
I	354	120.0	0.075	0.075	0.08	0.0766	1.16	1.16	5.3
		100.0	0.110	0.115	0.120	0.115	0.939	0.939	4.3
		80.4	0.190	0.190	0.190	0.190	0.721	0.721	3.92
		60.0	0.34	0.34	0.35	0.342	0.466	0.466	3.07
		40.2	0.57	0.57	0.57	0.57	0.244	0.244	2.2
		20.0	0.68	0.68	0.69	0.682	0.166	0.166	2.8
		8.0	0.83	0.83	0.83	0.830	0.081	0.081	3.42
II	354	120	0.07	0.07	0.07	0.07	1.155	1.155	5.2
		100	0.115	0.115	0.115	0.115	0.939	0.939	4.3
		80.4	0.20	0.195	0.195	0.1966	0.708	0.708	3.87
		60.0	0.345	0.35	0.35	0.348	0.458	0.458	2.99
		40.0	0.57	0.57	0.57	0.57	0.244	0.244	2.2
		20.0	0.685	0.685	0.69	0.686	0.166	0.166	2.89
		8.0	0.840	0.84	0.84	0.84	0.076	0.076	3.26
III	354	120.0	0.085	0.085	0.09	0.0866	1.063	1.063	4.57
		100.0	0.135	0.135	0.135	0.135	0.870	0.870	4.04
		80.0	0.20	0.20	0.20	0.20	0.699	0.699	3.74
		60.0	0.325	0.330	0.335	0.330	0.482	0.482	3.21
		40.0	0.57	0.575	0.575	0.573	0.241	0.241	2.19
		20.0	0.68	0.685	0.685	0.683	0.166	0.166	2.89
		8.0	0.790	0.790	0.790	0.790	0.102	0.102	4.36

TABLE XXV

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{BP} \rightleftharpoons [\text{ADDUCT}]$ in benzene VDEHPA concentration = 7.2 millimolar, equilibration time 3 hr. Temp. 23°C, D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	$K \text{ l mol}^{-1}$
			T_1	T_2	T_3				
I	350	160.0	0.090	0.090	0.090	0.090	1.046	0.894	2.8
		120.0	0.16	0.165	0.170	0.165	0.783	0.664	2.5
		100.0	0.23	0.23	0.23	0.23	0.638	0.538	2.25
		80.0	0.37	0.37	0.38	0.372	0.430	0.344	1.65
		40.0	0.64	0.64	0.64	0.64	0.194	0.154	1.37
		20.0	0.76	0.76	0.76	0.76	0.119	0.009	1.78
II	350	160.0	0.110	0.110	0.110	0.110	0.959	0.807	2.48
		120.0	0.20	0.20	0.20	0.20	0.699	0.580	2.17
		100.0	0.28	0.28	0.285	0.282	0.550	0.450	1.83
		80.0	0.46	0.45	0.47	0.47	0.337	0.251	1.16
		40.0	0.65	0.65	0.65	0.65	0.187	0.147	1.31
		20.0	0.74	0.74	0.74	0.74	0.127	0.107	1.86
III	350	160.0	0.110	0.115	0.115	0.113	0.947	0.795	2.41
		120.0	0.190	0.195	0.195	0.193	0.714	0.595	2.25
		100.0	0.275	0.275	0.28	0.276	0.559	0.459	1.88
		80.0	0.46	0.465	0.48	0.468	0.330	0.244	1.15
		40.0	0.665	0.67	0.67	0.668	0.175	0.135	1.20
		20.0	0.76	0.76	0.76	0.76	0.119	0.099	1.77

TABLE IV

Summary of the results of the tests of the various types of concrete beams under load. The values in parentheses are the values of the load at failure. The values in brackets are the values of the load at the time of the first crack. The values in the last column are the values of the load at the time of the first crack, expressed as a percentage of the load at failure.

Beam No.	Type	Span, ft.	Supports, in.	Load, lb.			Load at first crack, lb.	Load at failure, lb.	Load at first crack, % of load at failure
				1	2	3			
1	1	10	12	1000	1000	1000	1000	1000	100
2	1	10	12	1000	1000	1000	1000	1000	100
3	1	10	12	1000	1000	1000	1000	1000	100
4	1	10	12	1000	1000	1000	1000	1000	100
5	1	10	12	1000	1000	1000	1000	1000	100
6	1	10	12	1000	1000	1000	1000	1000	100
7	1	10	12	1000	1000	1000	1000	1000	100
8	1	10	12	1000	1000	1000	1000	1000	100
9	1	10	12	1000	1000	1000	1000	1000	100
10	1	10	12	1000	1000	1000	1000	1000	100
11	1	10	12	1000	1000	1000	1000	1000	100
12	1	10	12	1000	1000	1000	1000	1000	100
13	1	10	12	1000	1000	1000	1000	1000	100
14	1	10	12	1000	1000	1000	1000	1000	100
15	1	10	12	1000	1000	1000	1000	1000	100
16	1	10	12	1000	1000	1000	1000	1000	100
17	1	10	12	1000	1000	1000	1000	1000	100
18	1	10	12	1000	1000	1000	1000	1000	100
19	1	10	12	1000	1000	1000	1000	1000	100
20	1	10	12	1000	1000	1000	1000	1000	100
21	1	10	12	1000	1000	1000	1000	1000	100
22	1	10	12	1000	1000	1000	1000	1000	100
23	1	10	12	1000	1000	1000	1000	1000	100
24	1	10	12	1000	1000	1000	1000	1000	100
25	1	10	12	1000	1000	1000	1000	1000	100
26	1	10	12	1000	1000	1000	1000	1000	100
27	1	10	12	1000	1000	1000	1000	1000	100
28	1	10	12	1000	1000	1000	1000	1000	100
29	1	10	12	1000	1000	1000	1000	1000	100
30	1	10	12	1000	1000	1000	1000	1000	100
31	1	10	12	1000	1000	1000	1000	1000	100
32	1	10	12	1000	1000	1000	1000	1000	100
33	1	10	12	1000	1000	1000	1000	1000	100
34	1	10	12	1000	1000	1000	1000	1000	100
35	1	10	12	1000	1000	1000	1000	1000	100
36	1	10	12	1000	1000	1000	1000	1000	100
37	1	10	12	1000	1000	1000	1000	1000	100
38	1	10	12	1000	1000	1000	1000	1000	100
39	1	10	12	1000	1000	1000	1000	1000	100
40	1	10	12	1000	1000	1000	1000	1000	100
41	1	10	12	1000	1000	1000	1000	1000	100
42	1	10	12	1000	1000	1000	1000	1000	100
43	1	10	12	1000	1000	1000	1000	1000	100
44	1	10	12	1000	1000	1000	1000	1000	100
45	1	10	12	1000	1000	1000	1000	1000	100
46	1	10	12	1000	1000	1000	1000	1000	100
47	1	10	12	1000	1000	1000	1000	1000	100
48	1	10	12	1000	1000	1000	1000	1000	100
49	1	10	12	1000	1000	1000	1000	1000	100
50	1	10	12	1000	1000	1000	1000	1000	100
51	1	10	12	1000	1000	1000	1000	1000	100
52	1	10	12	1000	1000	1000	1000	1000	100
53	1	10	12	1000	1000	1000	1000	1000	100
54	1	10	12	1000	1000	1000	1000	1000	100
55	1	10	12	1000	1000	1000	1000	1000	100
56	1	10	12	1000	1000	1000	1000	1000	100
57	1	10	12	1000	1000	1000	1000	1000	100
58	1	10	12	1000	1000	1000	1000	1000	100
59	1	10	12	1000	1000	1000	1000	1000	100
60	1	10	12	1000	1000	1000	1000	1000	100
61	1	10	12	1000	1000	1000	1000	1000	100
62	1	10	12	1000	1000	1000	1000	1000	100
63	1	10	12	1000	1000	1000	1000	1000	100
64	1	10	12	1000	1000	1000	1000	1000	100
65	1	10	12	1000	1000	1000	1000	1000	100
66	1	10	12	1000	1000	1000	1000	1000	100
67	1	10	12	1000	1000	1000	1000	1000	100
68	1	10	12	1000	1000	1000	1000	1000	100
69	1	10	12	1000	1000	1000	1000	1000	100
70	1	10	12	1000	1000	1000	1000	1000	100
71	1	10	12	1000	1000	1000	1000	1000	100
72	1	10	12	1000	1000	1000	1000	1000	100
73	1	10	12	1000	1000	1000	1000	1000	100
74	1	10	12	1000	1000	1000	1000	1000	100
75	1	10	12	1000	1000	1000	1000	1000	100
76	1	10	12	1000	1000	1000	1000	1000	100
77	1	10	12	1000	1000	1000	1000	1000	100
78	1	10	12	1000	1000	1000	1000	1000	100
79	1	10	12	1000	1000	1000	1000	1000	100
80	1	10	12	1000	1000	1000	1000	1000	100
81	1	10	12	1000	1000	1000	1000	1000	100
82	1	10	12	1000	1000	1000	1000	1000	100
83	1	10	12	1000	1000	1000	1000	1000	100
84	1	10	12	1000	1000	1000	1000	1000	100
85	1	10	12	1000	1000	1000	1000	1000	100
86	1	10	12	1000	1000	1000	1000	1000	100
87	1	10	12	1000	1000	1000	1000	1000	100
88	1	10	12	1000	1000	1000	1000	1000	100
89	1	10	12	1000	1000	1000	1000	1000	100
90	1	10	12	1000	1000	1000	1000	1000	100
91	1	10	12	1000	1000	1000	1000	1000	100
92	1	10	12	1000	1000	1000	1000	1000	100
93	1	10	12	1000	1000	1000	1000	1000	100
94	1	10	12	1000	1000	1000	1000	1000	100
95	1	10	12	1000	1000	1000	1000	1000	100
96	1	10	12	1000	1000	1000	1000	1000	100
97	1	10	12	1000	1000	1000	1000	1000	100
98	1	10	12	1000	1000	1000	1000	1000	100
99	1	10	12	1000	1000	1000	1000	1000	100
100	1	10	12	1000	1000	1000	1000	1000	100

TABLE XXVI

Spectrophotometric determination of equilibrium constant of the reaction $\text{VDEHPA} + 4\text{EP} \rightleftharpoons [\text{ADDUCT}]$ VDEHPA concentration = 7.2 millimolar, equilibration time 3 hr. Temp. 23°C, D= Absorbance, D_c =corrected D, B=Base. Solvent, benzene.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K l mol^{-1}
			T_1	T_2	T_3				
I	346	160.0	0.03	0.03	0.03	0.03	1.523	1.523	6.5
		120.0	0.07	0.07	0.07	0.071	1.149	1.149	5.1
		80.0	0.21	0.21	0.21	0.021	0.678	0.678	3.14
		40.0	0.65	0.65	0.65	0.61	0.215	0.215	1.86
		20.0	0.765	0.770	0.775	0.77	0.114	0.114	1.97
		8.0	0.86	0.86	0.865	0.861	0.066	0.066	2.8
II	346	160.0	0.03	0.03	0.03	0.03	1.523	1.523	6.5
		120.0	0.075	0.075	0.08	0.0751	1.125	1.125	5.01
		100.0	0.145	0.150	0.150	0.148	0.830	0.830	3.94
		80.0	0.245	0.250	0.255	0.250	0.602	0.602	3.16
		40.0	0.655	0.655	0.66	0.656	0.184	0.184	1.8
		20.0	0.78	0.78	0.78	0.78	0.108	0.108	1.68
		8.0	0.92	0.92	0.92	0.92	0.92	0.036	1.5
III	346	160.0	0.03	0.03	0.03	0.03	1.523	1.523	6.5
		120.0	0.07	0.07	0.075	0.073	1.137	1.137	5.02
		100.0	0.130	0.140	0.140	0.133	0.876	0.876	4.06
		80.0	0.21	0.215	0.215	0.213	0.672	0.672	3.62
		40.0	0.63	0.63	0.64	0.633	0.134	0.134	1.15
		20.0	0.75	0.755	0.76	0.755	0.121	0.121	2.1
		8.0	0.855	0.855	0.855	0.855	0.069	0.069	2.96

TABLE XXVII

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{EP} \rightleftharpoons [\text{ADDUCT}]$ in hexane solutions. VDEHPA concentration 7.2 millimolar, equilibration time 3 hr. Temp. 23°C, D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	$K \text{ l mol}^{-1}$
			T_1	T_2	T_3				
I	346	160.0	0.31	0.31	0.31	0.310	0.509	0.509	1.29
		120.0	0.35	0.35	0.355	0.352	0.454	0.454	1.48
		80.0	0.52	0.52	0.52	0.520	0.284	0.284	1.34
		60.0	0.54	0.55	0.55	0.546	0.263	0.263	1.6
		40.0	0.60	0.605	0.605	0.603	0.220	0.220	1.98
		20.0	0.73	0.73	0.73	0.73	0.137	0.137	2.4
II	346	160.0	0.33	0.33	0.34	0.333	0.478	0.478	1.17
		120.0	0.38	0.38	0.38	0.380	0.420	0.420	1.39
		80.0	0.44	0.47	0.47	0.463	0.330	0.330	1.58
		60.0	0.52	0.54	0.535	0.532	0.274	0.274	1.68
		40.0	0.58	0.59	0.585	0.585	0.233	0.233	2.12
		20.0	0.71	0.71	0.71	0.710	0.149	0.149	2.61
III	346	120.0	0.38	0.38	0.38	0.38	0.420	0.420	1.36
		80.0	0.44	0.43	0.45	0.44	0.357	0.357	1.68
		60.0	0.48	0.52	0.52	0.506	0.296	0.296	1.83
		40.0	0.58	0.58	0.59	0.582	0.236	0.236	2.12
		20.0	0.69	0.68	0.70	0.690	0.161	0.161	2.84

TABLE XXVIII

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{BP} \rightleftharpoons [\text{ADDUCT}]$ in hexane solutions. VDEHPA concentration 7.2 millimoles/l, equilibrium time 3 hr, Temp. 23°C, D= Absorbance D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K l mol^{-1}
			T_1	T_2	T_3				
I	350	160.0	0.07	0.07	0.07	0.07	1.155	1.047	3.4
		120.0	0.11	0.11	0.11	0.11	0.959	0.862	2.8
		80.0	0.18	0.18	0.18	0.18	0.745	0.659	3.47
		60.0	0.22	0.22	0.22	0.22	0.658	0.582	3.96
		40.0	0.30	0.30	.30	0.30	0.523	0.467	4.5
		20.0	0.54	0.54	0.54	0.54	0.268	0.234	4.06
II	350	160.0	0.05	0.06	0.06	0.53	1.276	1.168	4.0
		120.0	0.12	0.11	0.12	0.113	0.947	0.850	2.5
		80.0	0.19	0.185	0.185	0.153	0.815	0.739	4.03
		60.0	0.22	0.22	0.22	0.22	0.658	0.582	3.96
		40.0	0.30	0.30	0.31	0.303	0.518	0.462	4.5
		20.0	0.54	0.54	0.54	0.54	0.268	0.234	4.06
III	350	120.0	0.09	0.09	0.09	0.09	1.046	0.236	4.05
		80.0	0.14	0.15	0.15	0.146	0.836	0.494	4.84
		60.0	0.20	0.20	0.20	0.20	0.699	0.623	4.3
		40.0	0.28	0.275	0.29	0.282	0.550	0.750	3.92
		20.0	0.535	0.54	0.54	0.538	0.270	0.949	3.84

TABLE XXIX

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + \text{beta-Collidine} \rightleftharpoons [\text{ADDUCT}]$ in hexane solutions. VDEHPA concentration 7.2 millimoles/l, equilibrium time 3 hr, Temp. 23°C, D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K 1 mol^{-1}
			T_1	T_2	T_3				
I	340	20.0	0.64	0.64	0.64	0.64	0.194	0.176	3.2
		40.0	0.54	0.54	0.54	0.54	0.268	0.257	2.36
		60.0	0.42	0.425	0.44	0.428	0.369	0.365	2.38
		80.0	0.35	0.34	0.34	0.342	0.466	0.457	1.35
		120.0	0.23	0.23	0.23	0.23	0.638	0.616	2.45
		160.0	0.15	0.16	0.16	0.156	0.807	0.771	2.24
II	340	20.0	0.60	0.60	0.61	0.603	0.220	0.202	3.71
		40.0	0.52	0.53	0.53	0.526	0.279	0.268	2.51
		60.0	0.40	0.41	0.41	0.406	0.392	0.388	2.54
		80.0	0.35	0.36	0.36	0.356	0.449	0.440	1.96
		120.0	0.21	0.23	0.22	0.220	0.658	0.636	2.33
		140.0	0.15	0.15	0.15	0.150	0.824	0.748	2.21
III	340	20.0	0.59	0.60	0.60	0.596	0.225	0.207	3.82
		40.0	0.48	0.49	0.48	0.483	0.316	0.305	2.9
		60.0	0.35	0.35	0.35	0.350	0.456	0.452	2.96
		80.0	0.23	0.24	0.24	0.236	0.627	0.623	3.35
		120.0	0.19	0.18	0.18	0.182	0.740	0.728	2.72

TABLE XXX

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{EP} \rightleftharpoons [\text{ADDUCT}]$ in CHCl_3 solution. VDEHPA concentration 7.2 millimoles/l, equilibrium time 3 hr, Temp. 23°C , D= Absorbance D_c =Corrected D, B=Base.

Expt. No.	Wave Length Milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K l mol^{-1}
			T_1	T_2	T_3				
I	346	60.0	0.06	0.05	0.05	0.052	1.284	1.284	3.2
		40.0	0.15	0.15	0.15	0.150	0.818	0.818	2.87
		24.0	0.47	0.47	0.49	0.476	0.322	0.322	1.34
		20.0	0.62	0.62	0.62	0.620	0.208	0.208	1.74
		12.0	0.74	0.74	0.75	0.743	0.129	0.129	1.36
II	346	60.0	0.04	0.04	0.05	0.043	1.367	1.367	3.4
		40.0	0.12	0.12	0.13	0.122	0.914	0.914	3.2
		24.0	0.47	0.49	0.50	0.486	0.314	0.314	1.77
		20.0	0.61	0.61	0.62	0.612	0.213	0.213	1.38
		32.0	0.19	0.19	0.19	0.19	0.721	0.721	3.18
		12.0	0.78	0.78	0.78	0.78	0.108	0.108	1.15
III	346	60.0	0.05	0.05	0.05	0.05	1.301	1.301	3.36
		40.0	0.134	0.14	0.14	0.133	0.876	0.876	3.12
		20.0	0.59	0.61	0.61	0.603	0.220	0.220	1.44
		12.0	0.78	0.78	0.77	0.776	0.110	0.110	1.16
		24.0	0.48	0.49	0.49	0.486	0.313	0.313	1.69
		32.0	0.21	0.21	0.21	0.21	0.678	0.678	2.95

TABLE XXXI

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{BP} \rightleftharpoons [\text{ADDUCT}]$ in CHCl_3 . VDEHPA concentration 7.2 millimoles/l, equilibrium time 3 hr, Temp. 23°C , D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K $l \text{ mol}^{-1}$
			T_1	T_2	T_3				
I	350	20.0	0.69	0.70	0.70	0.696	0.157	0.123	2.2
		40.0	0.355	0.34	0.35	0.348	0.458	0.392	4.02
		60.0	0.120	0.120	0.120	0.120	0.921	0.850	5.6
		12.0	0.82	0.82	0.82	0.82	0.086	0.072	2.1
		32.0	0.55	0.55	0.55	0.55	0.260	0.218	2.5
		48.0	0.21	0.21	0.21	0.21	0.678	0.612	5.7
II	350	20.0	0.69	0.69	0.70	0.696	0.157	0.123	2.2
		40.0	0.33	0.33	0.33	0.33	0.482	0.422	4.3
		60.0	0.12	0.12	0.12	0.12	0.921	0.850	5.6
		12.0	0.82	0.82	0.82	0.82	0.086	.072	2.1
		32.0	0.55	0.55	0.55	0.55	0.260	0.218	2.5
		48.0	0.23	0.23	0.23	0.23	0.638	0.572	5.2
III	350	20.0	0.69	0.69	0.690	0.690	0.161	0.127	2.3
		40.0	0.34	0.31	0.31	0.313	0.504	0.438	4.48
		60.0	0.12	0.12	0.12	0.12	0.921	0.850	5.6
		12.0	0.86	0.86	0.86	0.86	0.066	0.048	1.35
		32.0	0.56	0.57	0.57	0.566	0.247	0.205	2.38
		48.0	0.23	0.23	0.23	0.638	0.638	0.567	5.3

TABLE XXXII

Spectrophotometric determination of the equilibrium constant (K) of the reaction $\text{VDEHPA} + 4\text{IPP} \rightleftharpoons [\text{ADDUCT}]$ in CHCl_3 solution. VDEHPA concentration 7.2 millimolar, equilibrium time 3 hr, Temp. 23°C . D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K l mol^{-1}
			T_1	T_2	T_3				
I	354	20.0	0.580	0.590	0.595	0.585	0.233	0.233	1.5
		40.0	0.150	0.150	0.160	0.156	0.807	0.807	2.85
		60.0	0.06	0.06	0.06	0.06	1.222	1.222	3.1
		12.0	0.78	0.78	0.79	0.786	0.104	0.104	1.1
		32.0	0.34	0.35	0.36	0.35	0.456	0.456	1.68
		48.0	0.12	0.13	0.13	0.126	0.900	0.900	2.7
II	354	20.0	0.580	0.580	0.590	0.586	0.232	0.232	1.52
		40.0	0.150	0.160	0.160	0.156	0.807	0.807	2.85
		60.0	0.060	0.070	0.070	0.066	1.181	1.181	2.54
		12.0	0.790	0.790	0.790	0.790	0.102	0.102	1.09
		32.0	0.29	0.30	0.31	0.30	0.523	0.523	2.26
		48.0	0.10	0.10	0.105	0.101	0.996	0.996	3.04
III	354	20.0	0.580	0.580	0.580	0.580	0.237	0.237	1.51
		40.0	0.140	0.150	0.150	0.145	0.839	0.839	2.98
		60.0	0.060	0.060	0.060	0.060	1.222	1.222	3.10
		12.0	0.780	0.775	0.790	0.788	0.109	1.09	1.16
		32.0	0.310	0.320	0.340	0.325	0.489	0.489	2.06
		48.0	0.10	0.10	0.10	0.100	1.00	1.00	3.04

TABLE XXXIII

Spectrophotometric determination of the equilibrium constant (K) of the reaction VDEHPA + beta-Collidine \rightleftharpoons [ADDUCT] in CHCl_3 solutions. VDEHPA concentration 7.2 millimoles/l, equilibrium time 3 hr, Temp. 23°C , D= Absorbance, D_c =Corrected D, B=Base.

Expt. No.	Wave Length milli-microns	Concn. of Base milli-moles/l	Transmittances			Average T	D	D_c	K l mol^{-1}
			T_1	T_2	T_3				
I	340	8.0	0.770	0.770	0.770	0.770	0.114	0.110	1.78
		16.0	0.285	0.295	0.295	0.290	0.538	0.520	4.66
		24.0	0.090	0.090	0.090	0.092	1.036	1.009	6.10
		32.0	0.060	0.050	0.050	0.056	1.252	1.213	6.2
II	340	8.0	0.770	0.770	0.770	0.770	0.114	0.110	1.78
		16.0	0.275	0.290	0.300	0.288	0.541	0.523	4.7
		24.0	0.08	0.090	0.09	0.086	1.066	1.039	6.4
		32.0	0.05	0.05	0.05	0.05	1.301	1.262	5.3
III	340	8.0	0.750	0.750	0.75	0.750	0.125	0.121	2.02
		16.0	0.250	0.250	0.25	0.250	0.602	0.584	5.3
		32.0	0.050	0.050	0.050	0.050	1.301	1.262	6.12
		24.0	0.090	0.090	0.090	0.090	1.046	1.019	6.6

TABLE XXXIV

Absorbances of beta-Collidine in different solvents.

Solvent	Wave Length milli- microns	Concn. of Base milli- moles/l	Transmittances			Aver- age T	D
			T ₁	T ₂	T ₃		
Benzene	340	160.0	0.620	0.620	0.620	0.62	0.208
		120.0	0.680	0.680	0.680	0.68	0.168
		100.0	0.720	0.720	0.725	0.722	0.141
		80.0	0.750	0.750	0.750	0.75	0.125
		40.0	0.850	0.850	0.860	0.852	0.070
		20.0	0.940	0.940	0.940	0.940	0.027
Hexane	340	20.0	0.96	0.96	0.96	0.96	0.018
		40.0	0.99	0.96	0.98	0.976	0.011
		60.0	0.99	0.99	0.99	0.99	0.004
		80.0	0.98	0.08	0.98	0.98	0.009
		120.0	0.95	0.95	0.95	0.95	0.022
		160.0	0.93	0.92	0.92	0.922	0.036
Chloroform	340	60.0	0.85	0.85	0.85	0.85	0.071
		48.0	0.86	0.86	0.86	0.86	0.066
		40.0	0.86	0.86	0.86	0.86	0.066
		32.0	0.90	0.91	0.915	0.908	0.042
		20.0	0.92	0.93	0.93	0.926	0.034
		12.0	0.96	0.96	0.96	0.96	0.018

TABLE XXXV

Absorbances of 4BP in different solvents.

Solvents	Wave Length milli- microns	Concn. of Base milli- moles/l	Transmittances			Aver- age T	D
			T ₁	T ₂	T ₃		
Benzene	350	160.0	0.705	0.705	0.705	0.705	0.152
		120.0	0.760	0.760	0.760	0.760	0.119
		100.0	0.790	0.790	0.80	0.793	0.100
		80.0	0.82	0.82	0.82	0.82	0.086
		40.0	0.91	0.91	0.915	0.912	0.040
		20.0	0.95	0.95	0.965	0.955	0.020
Hexane	350	160.0	0.78	0.78	0.78	0.78	0.108
		120.0	0.80	0.80	0.80	0.80	0.097
		80.0	0.82	0.82	0.82	0.82	0.086
		60.0	0.84	0.84	0.84	0.84	0.076
		40.0	0.87	0.88	0.88	0.88	0.056
		20.0	0.92	0.93	0.93	0.926	0.034
Chloroform	350	60.0	0.850	0.850	0.850	0.850	0.071
		48.0	0.860	0.860	0.860	0.860	0.066
		40.0	0.860	0.860	0.860	0.860	0.066
		32.0	0.900	0.915	0.910	0.908	0.042
		20.0	0.920	0.930	0.930	0.926	0.034
		12.0	0.960	0.960	0.960	0.960	0.018

TABLE XXXVI

Experimental IR Spectral Data

Compound		Frequency cm^{-1}	Assignment
1. VDEHPA in benzene	(a)	1205-10 1235-41	P=O stretching
	(b)	1440 1375	CH ₃ deformation CH ₂ scissor CH ₃ symmetrical vibration.
	(c)	930	V=O stretching
	(d)	880	CH ₃ wagging
	(e)	330, 485	P-O-V stretching
2. VDEHPA in hexane	(a)	1205, 1235	P=O stretching
	(b)	1130	C-O-P vibration
	(c)	930	V=O vibration
	(d)	875	CH ₃ wagging
	(e)	330, 490, 595	P-O-V stretch
3. 2.5% VDEHPA in 0.2M 4BP in hexane	(a)	1675, 1615	Pyridine ring stretching.
	(b)	1205, 1235	P=O stretch
	(c)	1125	C-O-[P] stretch
	(d)	930	V=O stretch
	(e)	875	CH ₃ wagging
	(f)	600, 540, 475, 325	V-O-P vibration

TABLE XXXVI (cont'd)

Compound	Frequency cm^{-1}	Assignment
4. 2.5% VDEHPA in 0.2M 4EP in hexane solution	(a) 1620	Pyridine ring stretching
	(b) 1210, 1235	P=O stretch
	(c) 1125	C-O-P stretch
	(d) 930	V=O stretch
	(e) 875	CH ₃ wagging
	(f) 595, 490, 330	V-O-P
5. 2.5% VDEHPA in 0.2M 2BP in hexane solution	(a) 1210, 1235	P=O stretch
	(b) 935	V=O stretch
	(c) 870	CH ₃ wagging
	(d) 595, 490, 330	V-O-P
6. 2.5% VDEHPA in 0.2M 4IPP in benzene solution	(a) 1615	Pyridine ring stretching
	(b) 1425	CH ₃ deformation
	1375	CH ₃ symmetrical vibration
	(c) 1210, 1235	P=O stretch
	(d) 1150	C-O-[P]
	(e) 930	V=O stretch
	(f) 875	CH ₃ wagging
	(g) 480, 325, 595	V-O-P

TABLE XXXVI (cont'd)

Compound		Frequency cm^{-1}	Assignment
7. 2.5% VDEHPA in 0.2M 2EP in benzene solution	(a)	1210, 1235	P=O stretch
	(b)	1440, 1375	CH ₃ deformation CH ₃ symmetrical vibration
	(c)	1150	C-O-[P]
	(d)	935	V=O stretch
	(e)	880	CH ₃ wagging
	(f)	480, 330	V-O-P stretch
8. 2.5% VDEHPA in 0.2M beta- Collidine in benzene solution	(a)	1622	Pyridine ring vibration
	(b)	1425, 1375	CH ₃ deformation CH ₃ symmetrical vibration
	(c)	1215, 1235	P=O stretch
	(d)	930	V=O stretch
	(e)	875, 785	CH ₃ wagging
	(f)	500, 470, 330	V-O-P stretch
9. 1% VDEHPA in 4IPP	(a)	1030, 1075	Unassigned
	(b)	950±2, 975	V=O stretch
	(c)	1250, 1280	P=O stretch

TABLE XXXVI (cont'd)

Compound	Frequency cm^{-1}	Assignment
10. 1% VDEHPA in 4EP	(a) 1030	Unassigned
	(b) 950	V=O stretch
	(c) 860	CH_3 wagging
	(d) 1230 ± 2	P=O stretch
11. 1% VDEHPA in 4BP	(a) 1040, 1090	Unassigned
	(b) 950	V=O stretch
	(c) 1240	P=O stretch
	(d) 865	CH_3 wagging
12. 1% VDEHPA in 2EP	(a) 1015, 1075	Unassigned
	(b) 930	V=O stretch
	(c) 870	CH_3 wagging
	(d) 1230	P=O stretch
13. 1% VDEHPA in beta- Collidine	(a) 1030, 1080	Unassigned
	(b) 950	V=O stretch
	(c) 862	CH_3 wagging
	(d) 1240	P=O stretch

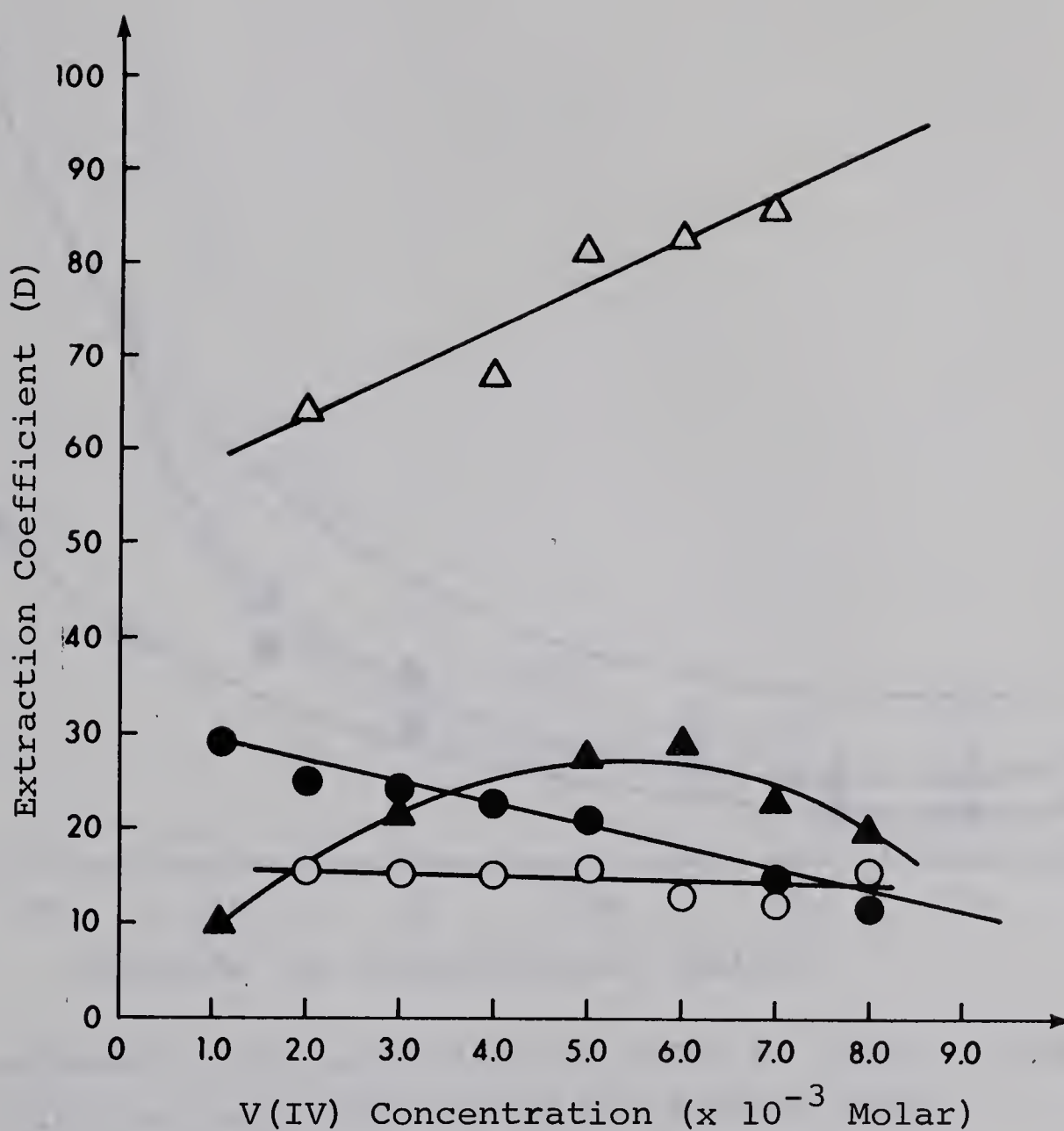


Fig.1. Dependence of the extraction coefficient on the V(IV) concentration in aq. phase.

DEHPA concentrations:- Open triangle 0.4 Molar, eq. pH 2.0 ± 0.2 ; closed triangle 0.3 Molar, eq. pH 1.7 ± 0.1 ; closed circle 0.1 Molar, eq. pH 1.9 ± 0.1 ; open circle 0.2 Molar, eq. pH 1.6.

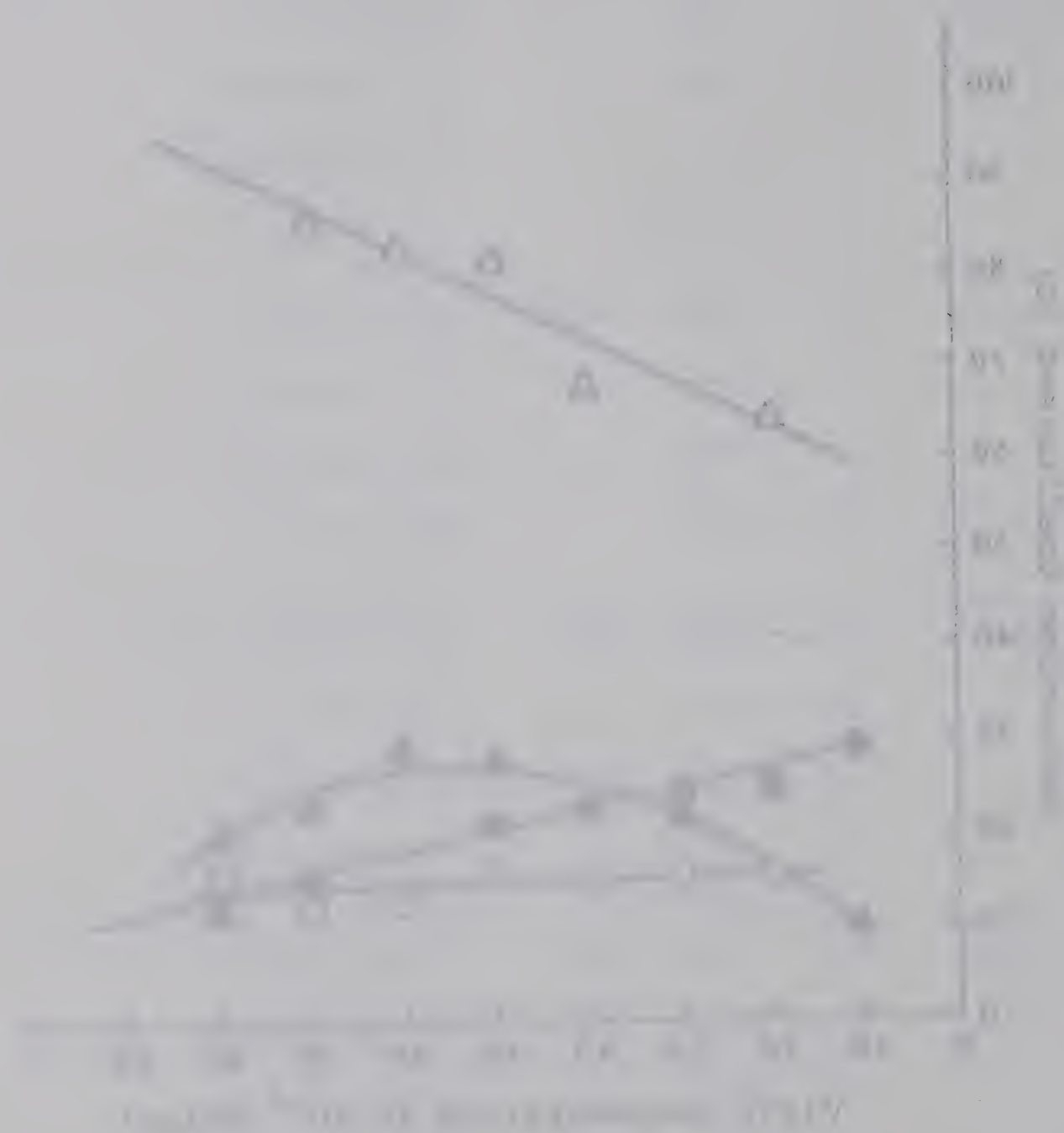


Fig. 1. Dependence of the properties of the solutions on the concentration of the solutions.

The properties of the solutions were determined by the following methods: the refractive index was measured by a refractometer, the density by a densimeter, the viscosity by a viscometer, and the surface tension by a tensiometer.

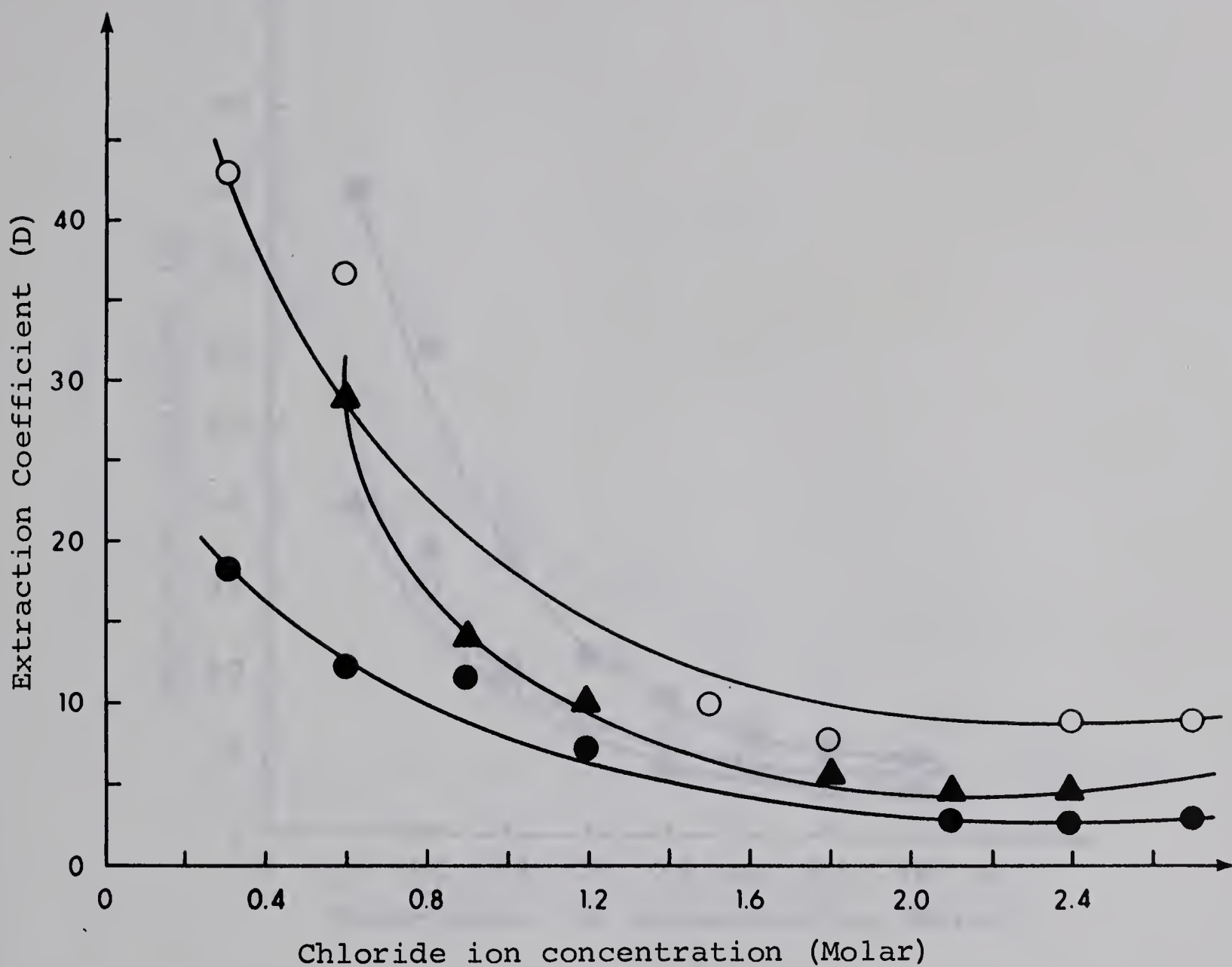


Fig.2. Dependence of the extraction of V(IV) by DEHPA on the chloride ion concentration in the aqueous phase. Open circle, initial pH 2.6; closed triangle, initial pH 4.1; closed circle, initial pH 3.0 ± 0.1 .

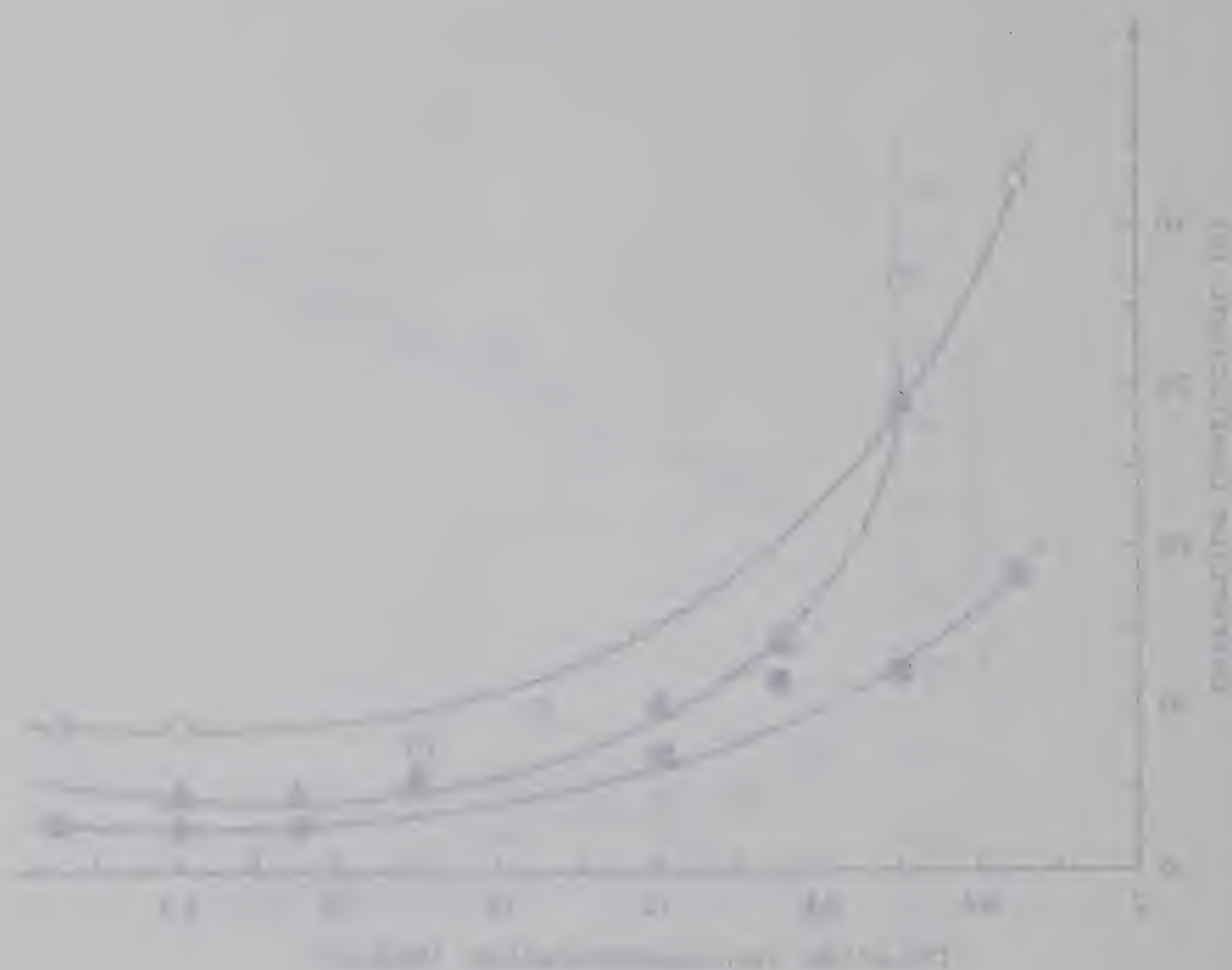


Fig. 1. Dependence of the rate of polymerization on the concentration of the monomer. The curves were obtained from the experimental data. The points represent the calculated values. The curves were obtained from the experimental data. The points represent the calculated values. The curves were obtained from the experimental data. The points represent the calculated values.

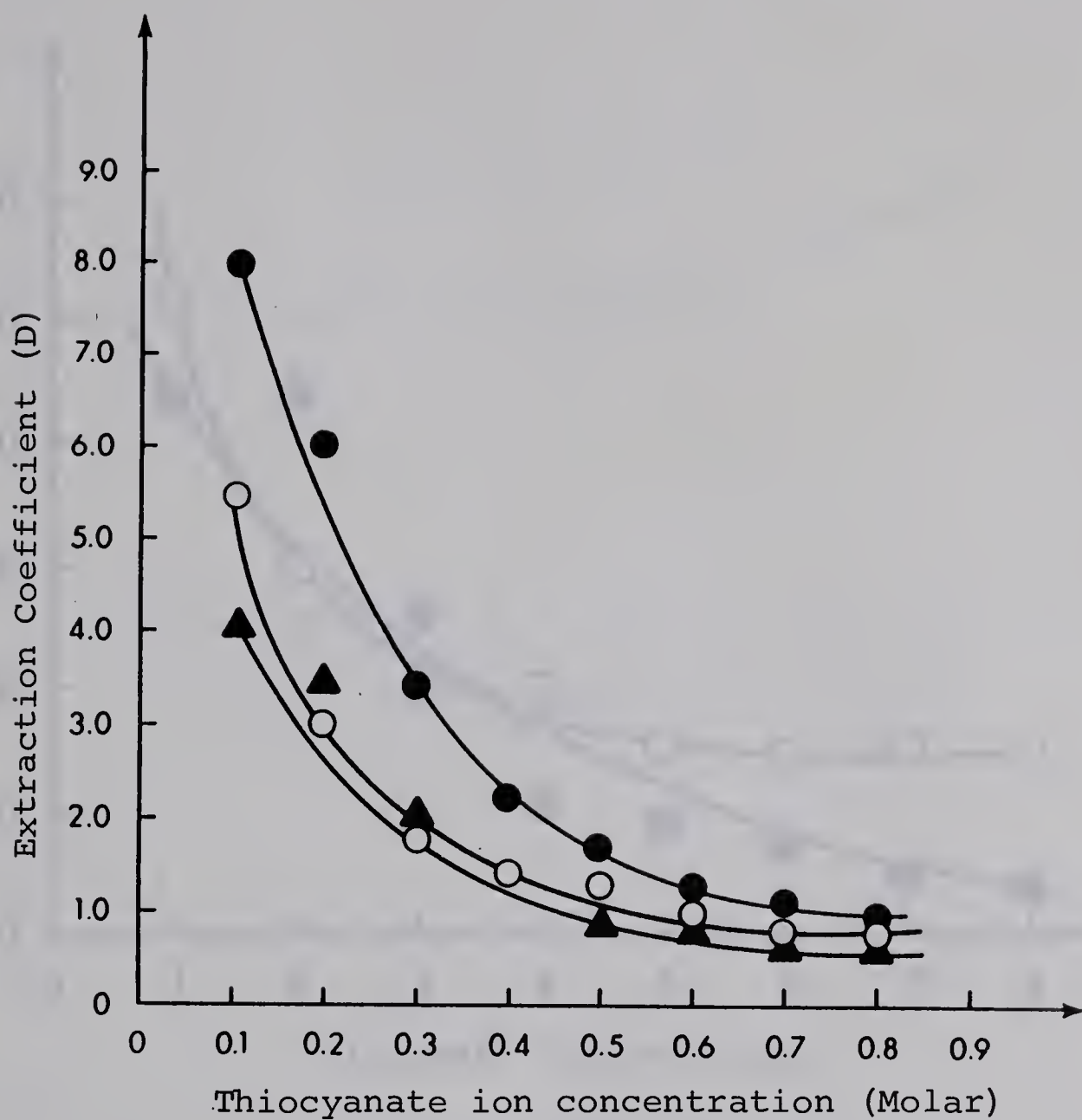


Fig.3(a) . Dependence of the V(IV) extraction on the thiocyanate ion concentration in the aq. phase. DEHPA concentration 0.1 Molar. Initial V(IV) concentration 10^{-2} Molar. Closed circle, initial pH 3.1, eq. pH 2.0 ± 0.1 ; open circle, initial pH 2.5, eq. pH 1.9 ± 0.1 ; closed triangle, initial pH 4.5, final pH 2.0.

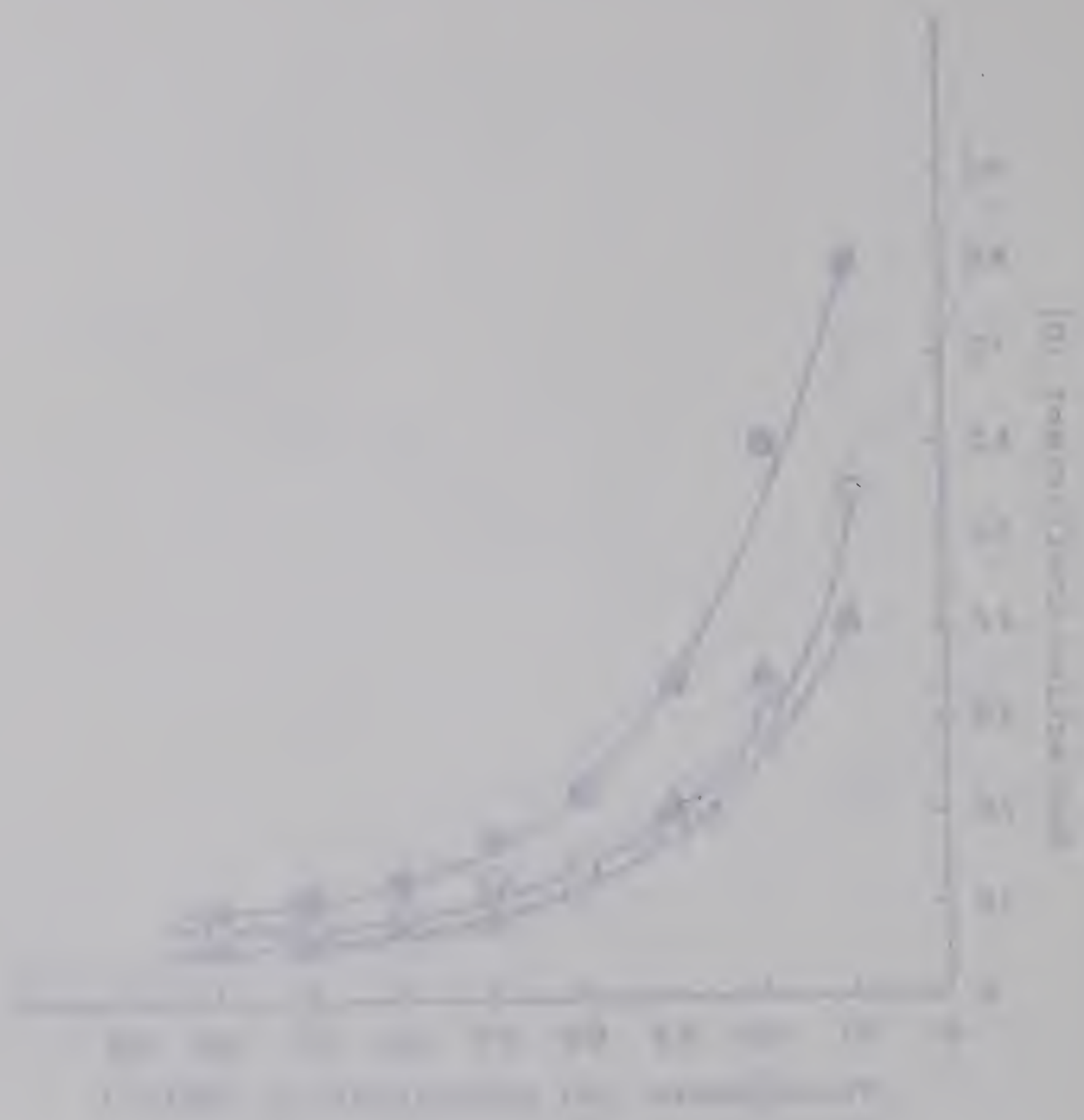


Fig. 1. Relationship between the concentration of a solution and its refractive index. The curves are for different solutions of the same substance in the same solvent. The refractive index increases with concentration.

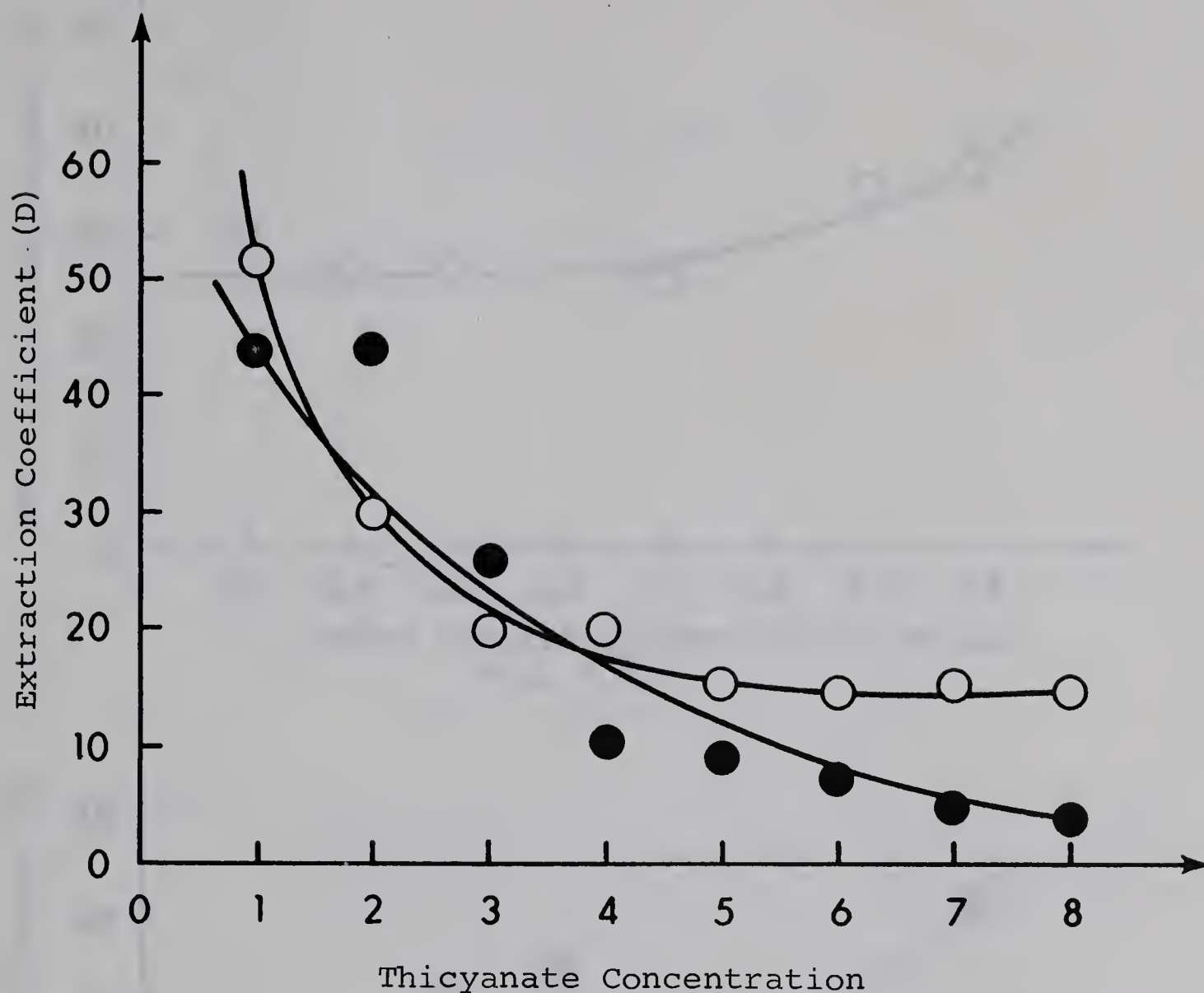
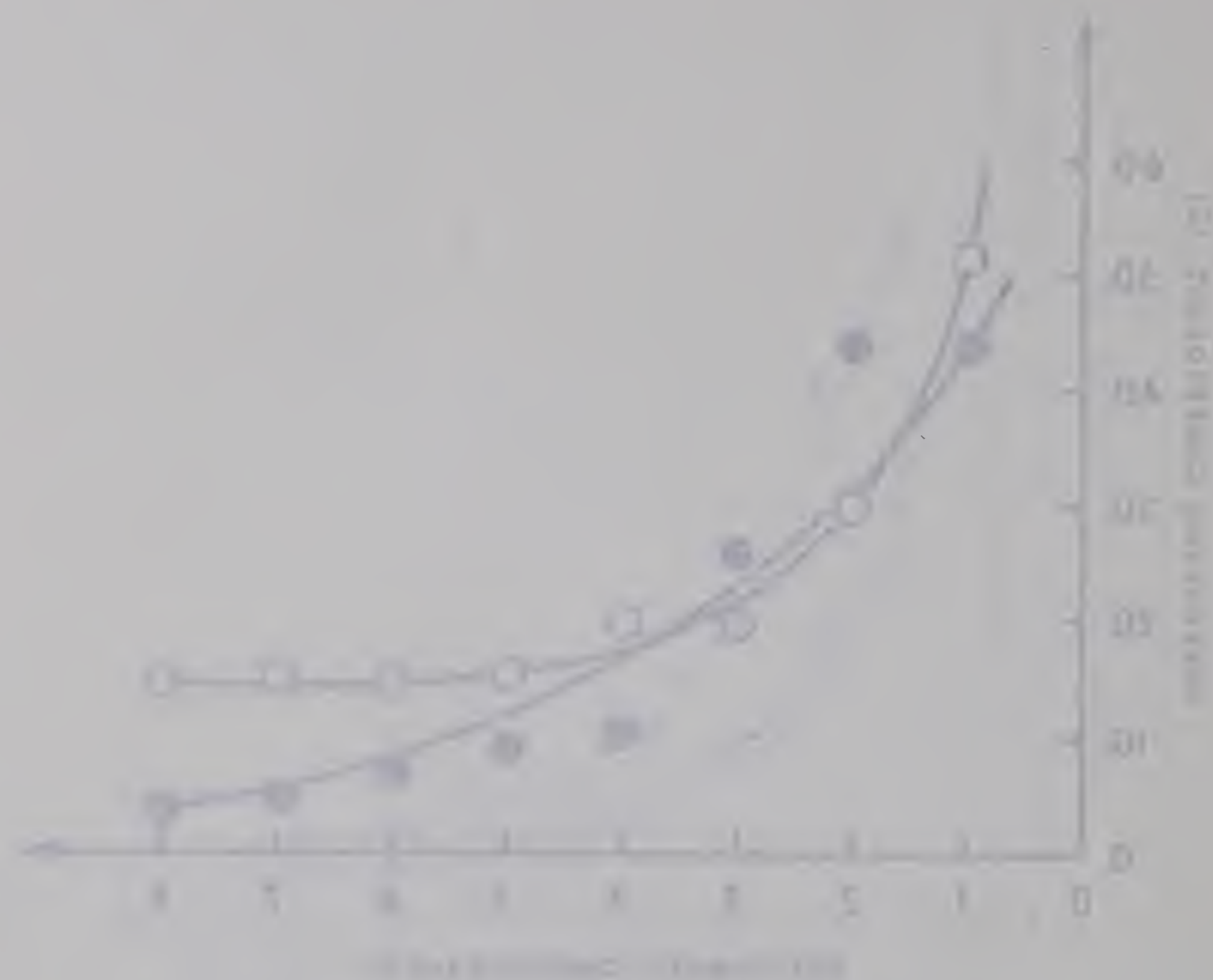


Fig.3(b) . Dependence of extraction on the thiocyanate ion concentration in aqueous phase.

Closed circle - thiocyanate concentration scale 10^{-1} Molar; initial V(IV) concentration 10^{-2} Molar, eq. pH 1.9.

Open circle - thiocyanate concentration 10^{-3} Molar; initial V(IV) concentration 10^{-3} Molar, eq. pH 2.55.



The rate of polymerization was measured by the method of ^{13}C NMR spectroscopy. The reaction was carried out in a sealed tube at 100°C for 24 hours. The concentration of the initiator was varied from 10^{-2} to 10^{-1} M. The rate of polymerization was determined from the change in the concentration of the monomer over time. The data are plotted in Figure 1. The rate of polymerization increases with the concentration of the initiator. The rate of polymerization is higher for the filled circles than for the open circles.

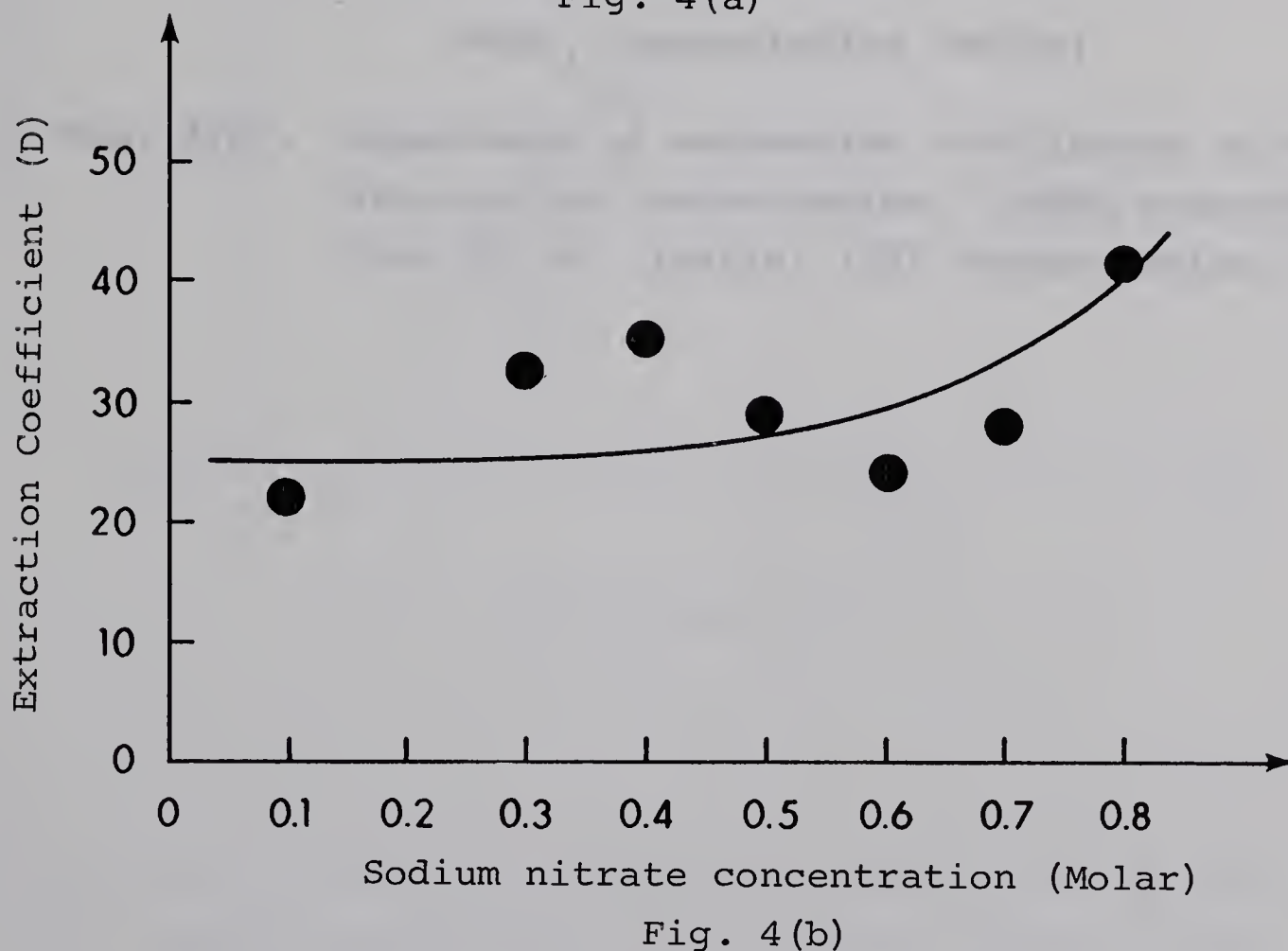
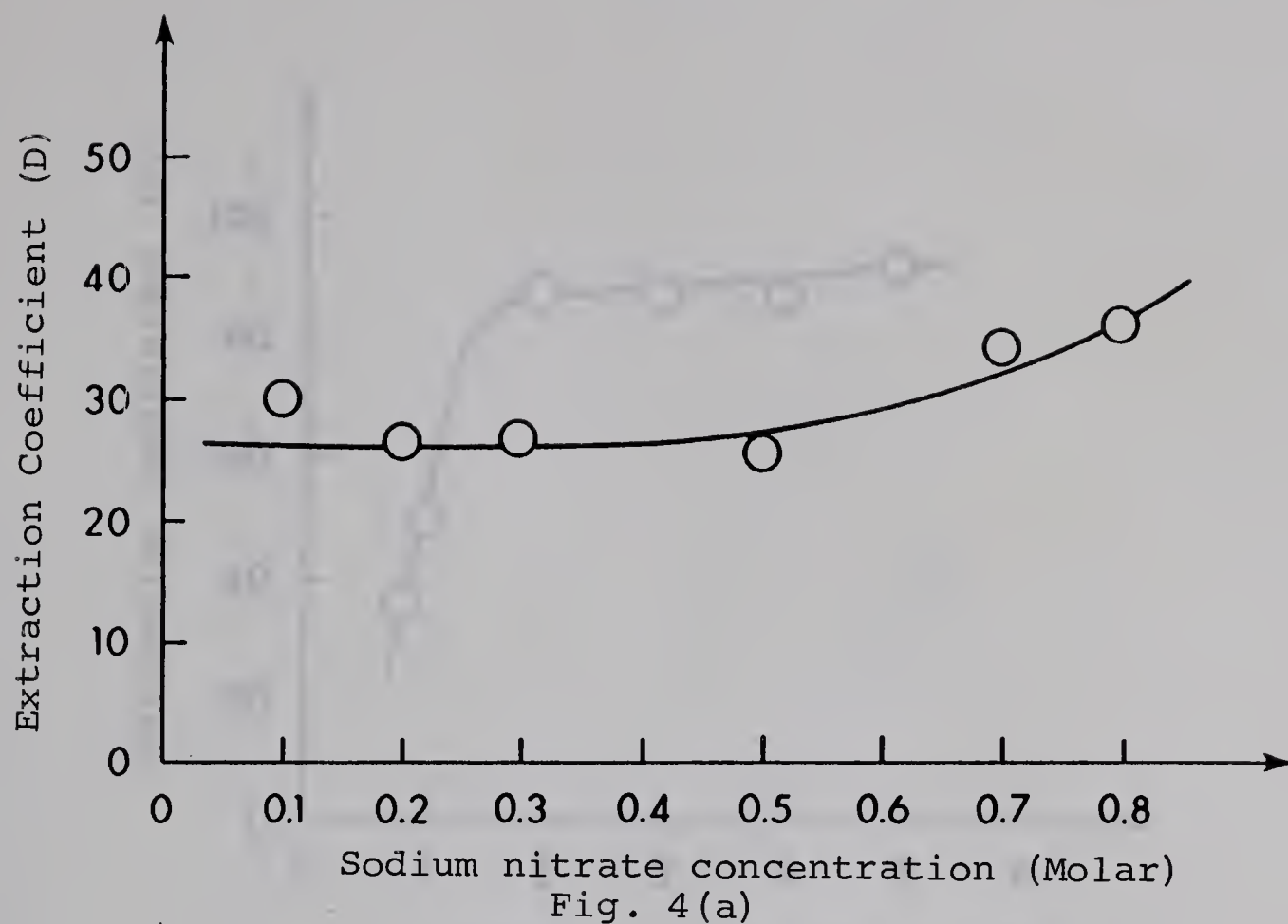


Fig.4(a) and (b). Dependence of extraction coefficient of V(IV) on the nitrate ion concentration in the aqueous phase. DEHPA concentration 0.1 Molar. Closed circle, initial V(IV) concentration 10^{-2} Molar, eq.pH 1.9; open circle, initial V(IV) concentration 10^{-3} Molar, eq. pH 2.5.

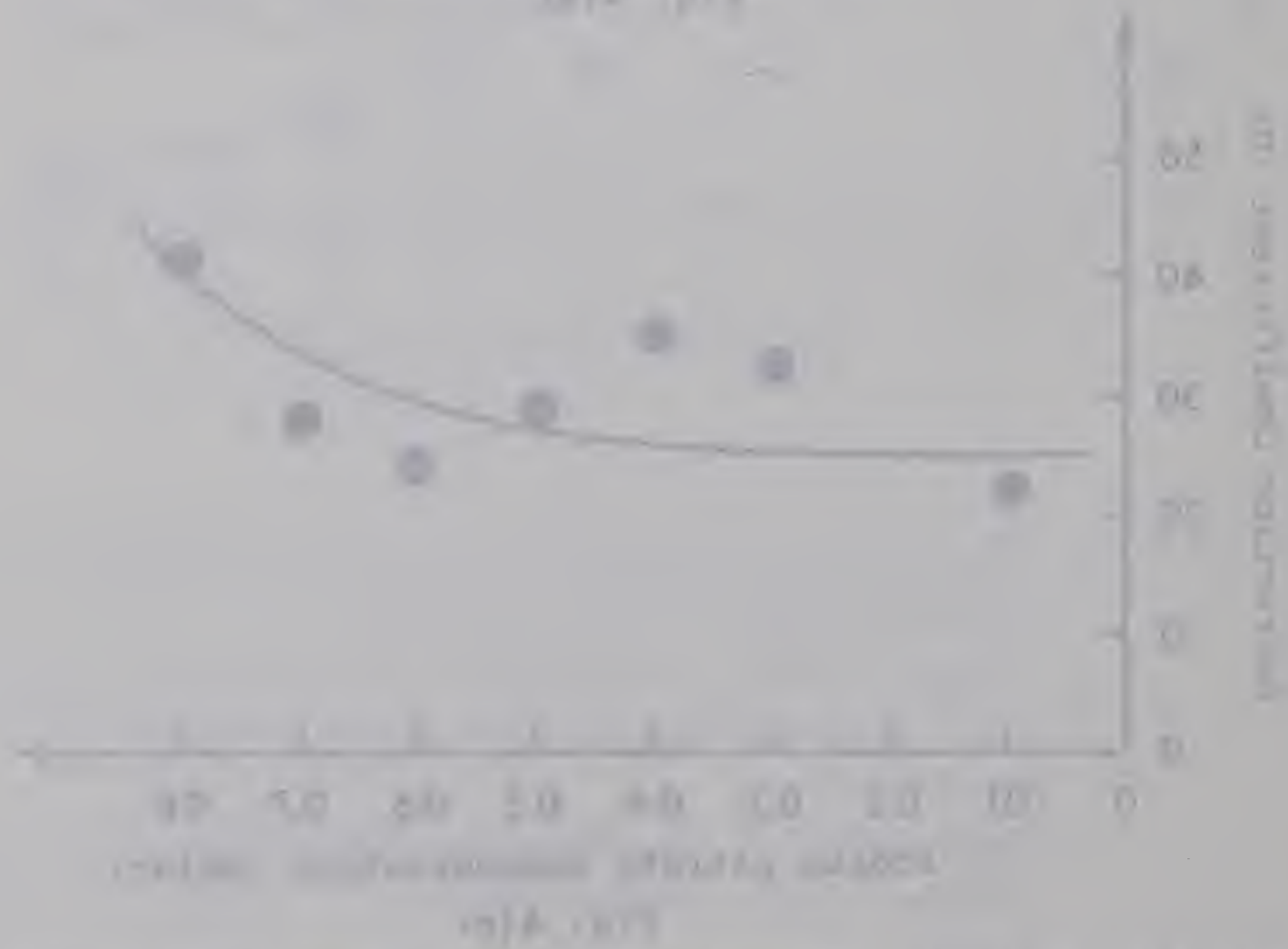
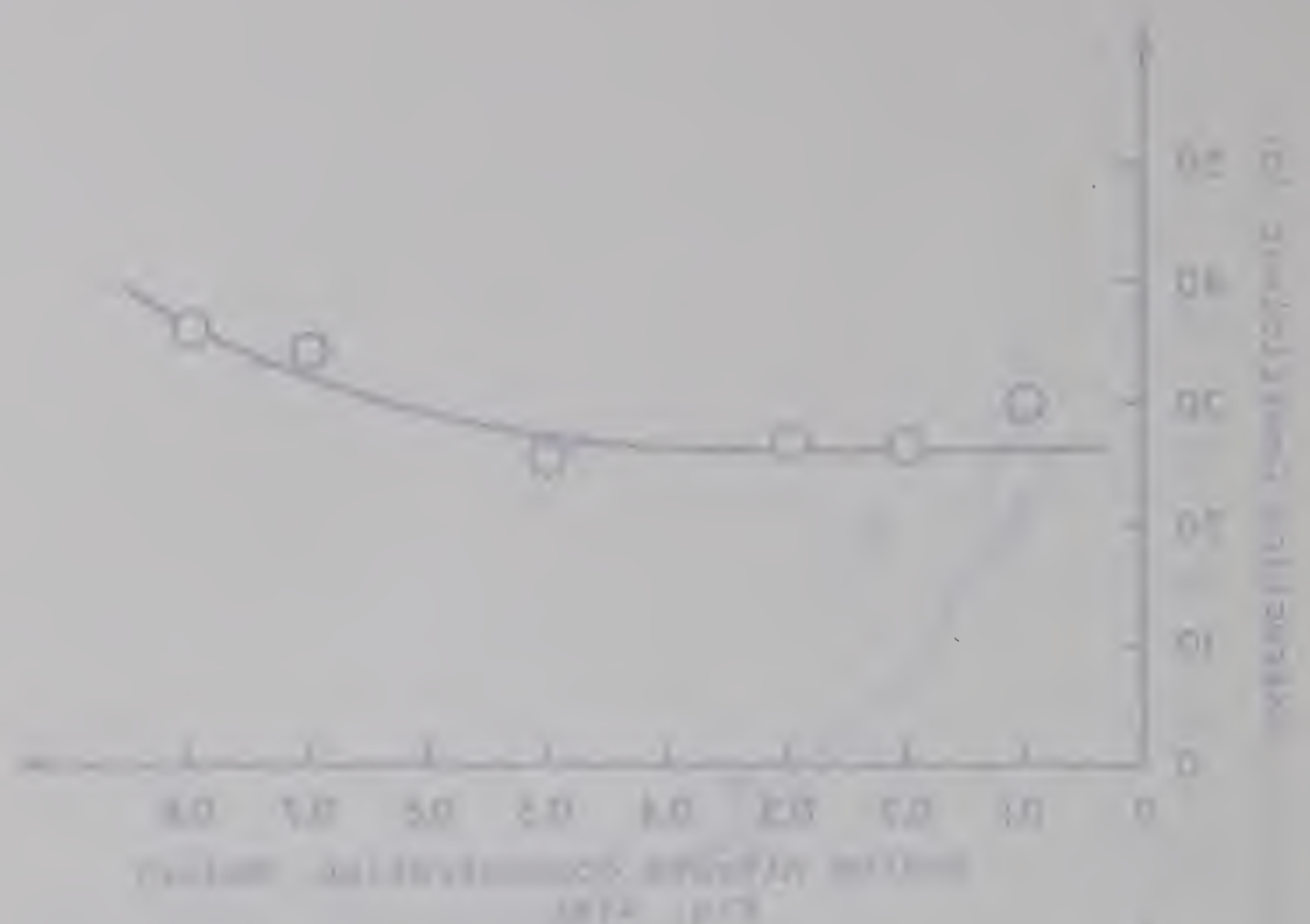


Fig. 2. Dependence of the degree of polymerization (P_n) on the initial concentration of monomer (M_0) for the polymerization of styrene in the presence of $AlCl_3$ and $AlEt_3$ (a) and $AlCl_3$ and $AlEt_3$ (b) at $25^\circ C$. The initial concentration of $AlCl_3$ was 0.01 mole/l. The initial concentration of $AlEt_3$ was 0.01 mole/l. The initial concentration of styrene was 0.1 mole/l. The initial concentration of $AlCl_3$ and $AlEt_3$ was 0.01 mole/l. The initial concentration of styrene was 0.1 mole/l. The initial concentration of $AlCl_3$ and $AlEt_3$ was 0.01 mole/l. The initial concentration of styrene was 0.1 mole/l.

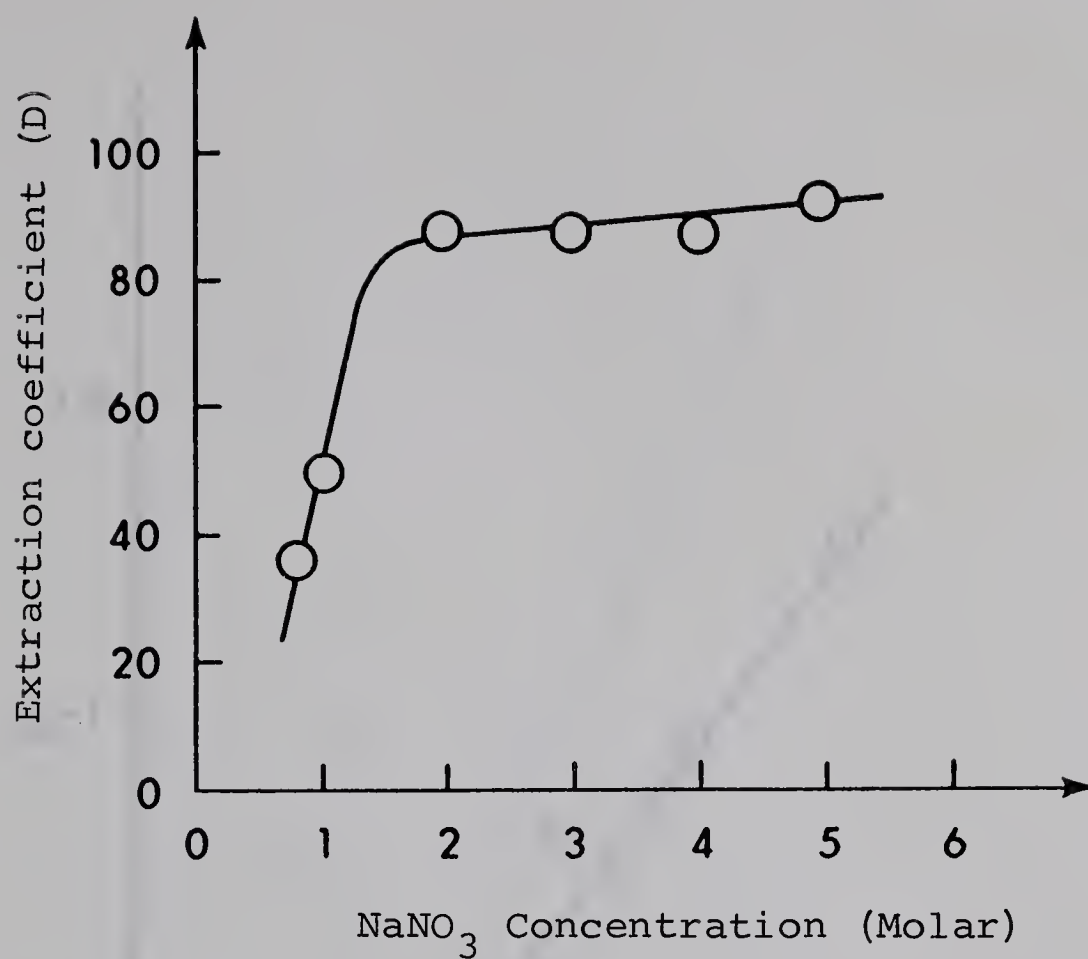


Fig. 4(c). Dependence of extraction coefficient on the Nitrate ion concentration. DEHPA concentration 0.1 M. Initial (IV) concentration 10^{-2} M.

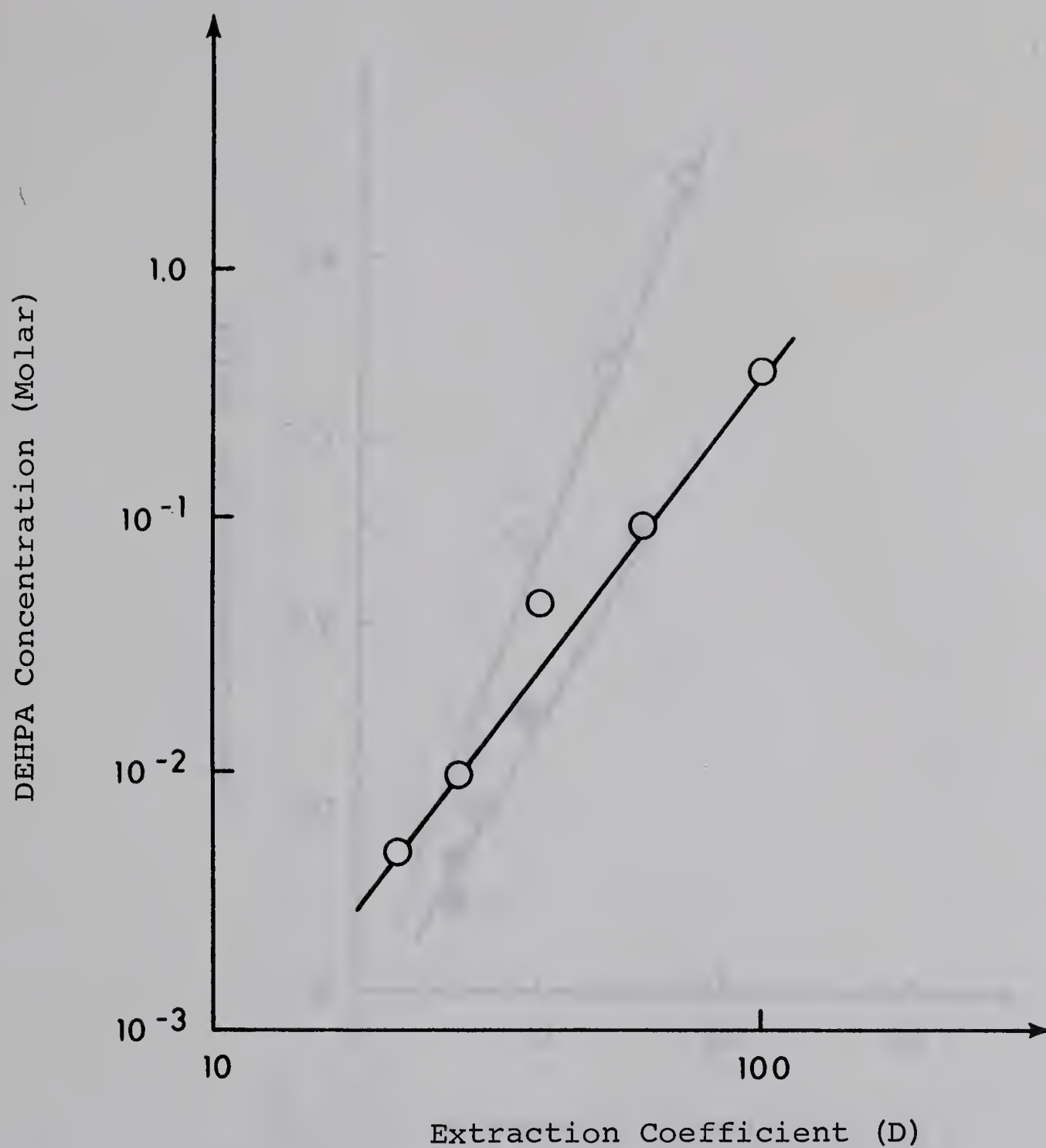


Fig.5. Dependence of the extraction coefficient on the DEHPA concentration in the organic phase. V(IV) concentration 5×10^{-4} Molar. pH 2.85.

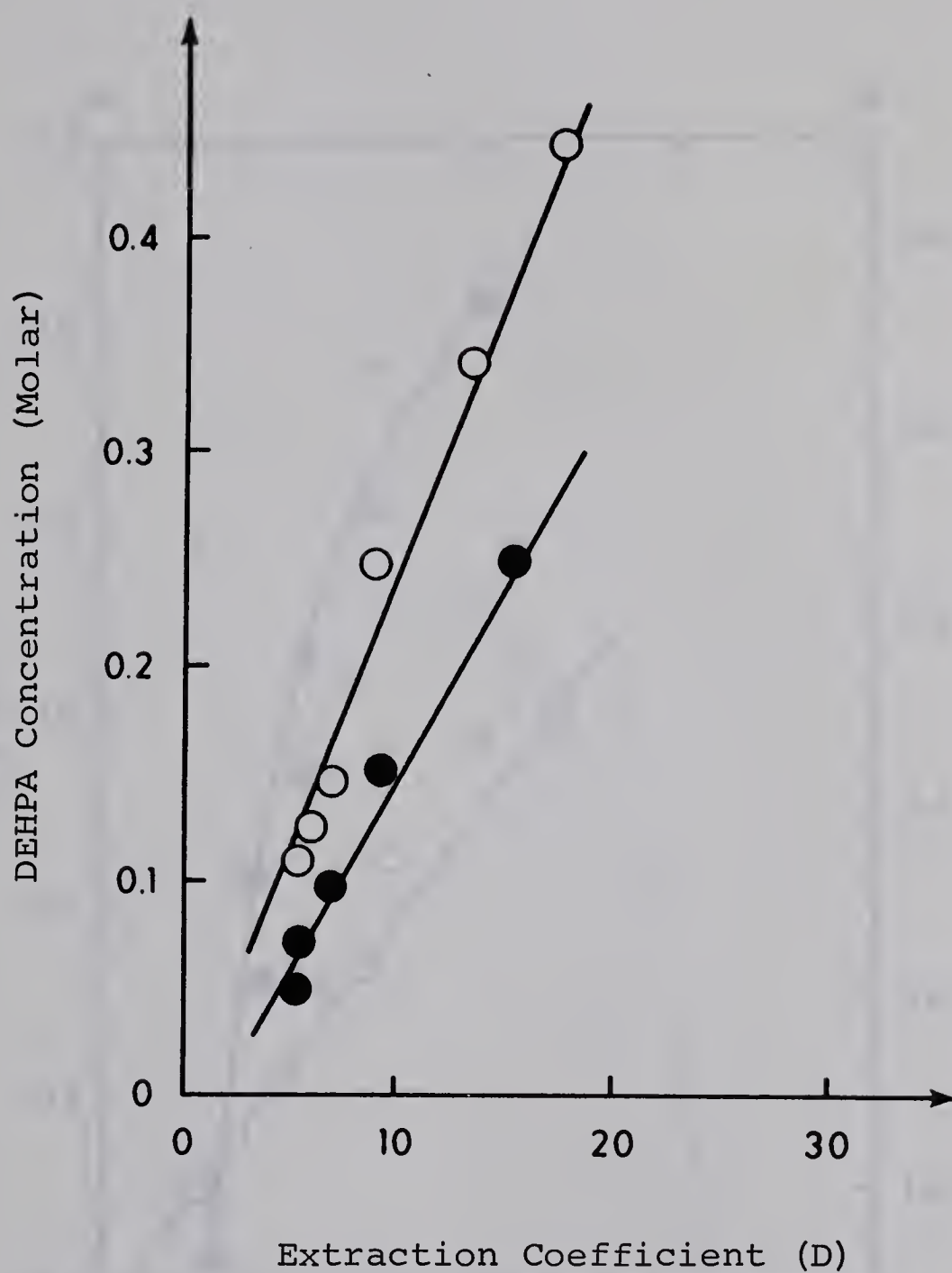


Fig.6. Dependence of the extraction coefficient on the DEHPA concentration in the organic phase.
Open circle pH 1.55; closed circle pH 1.43.
Initial V(IV) concentration 5×10^{-3} M.

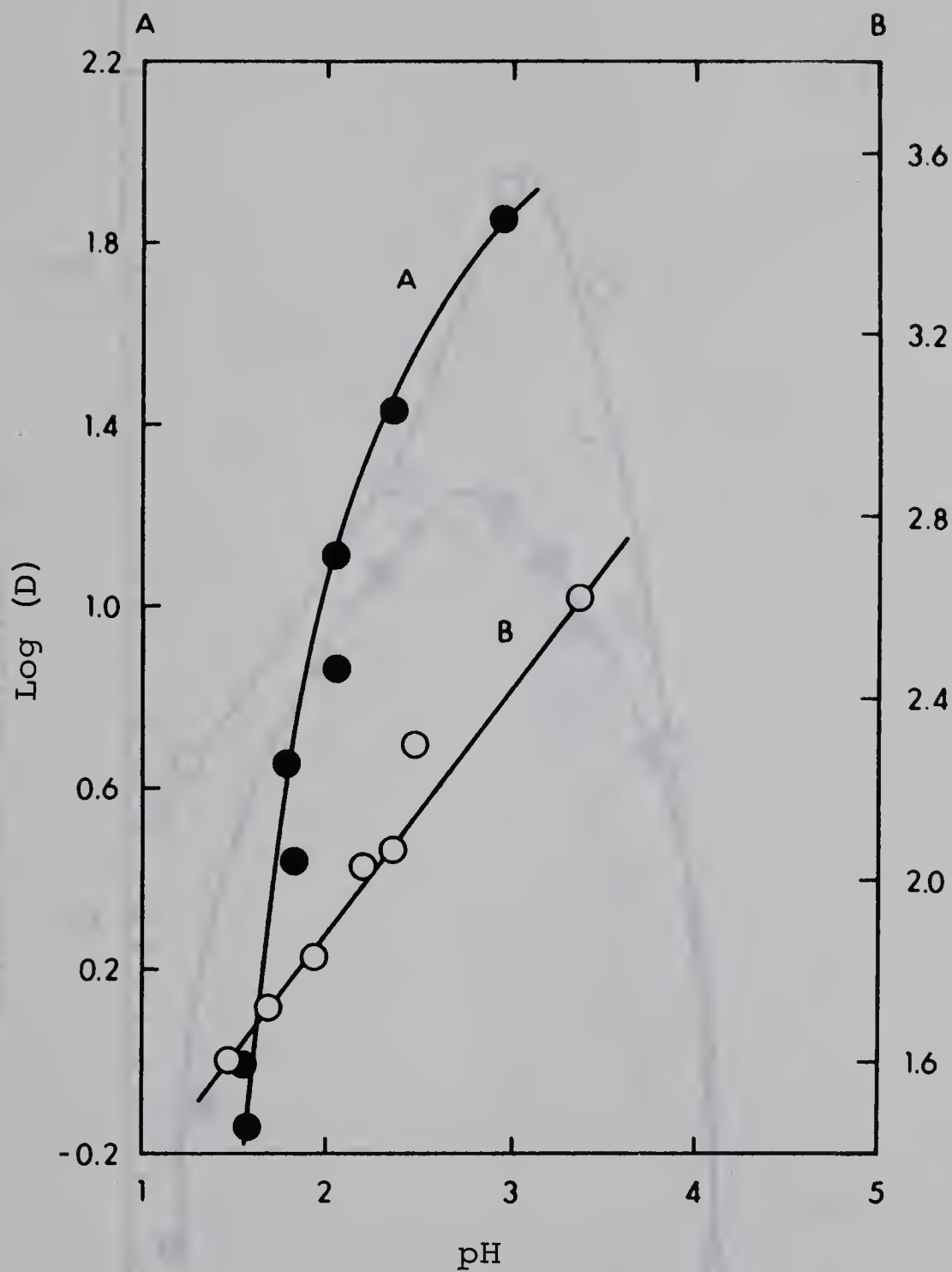


Fig.7. Dependence of the extraction of V(IV) by DEHPA on pH at low and high DEHPA concentrations. Closed circle 0.05 Molar DEHPA; open circle 0.4 Molar DEHPA. Initial aq. V(IV) concentration 5×10^{-3} Molar.

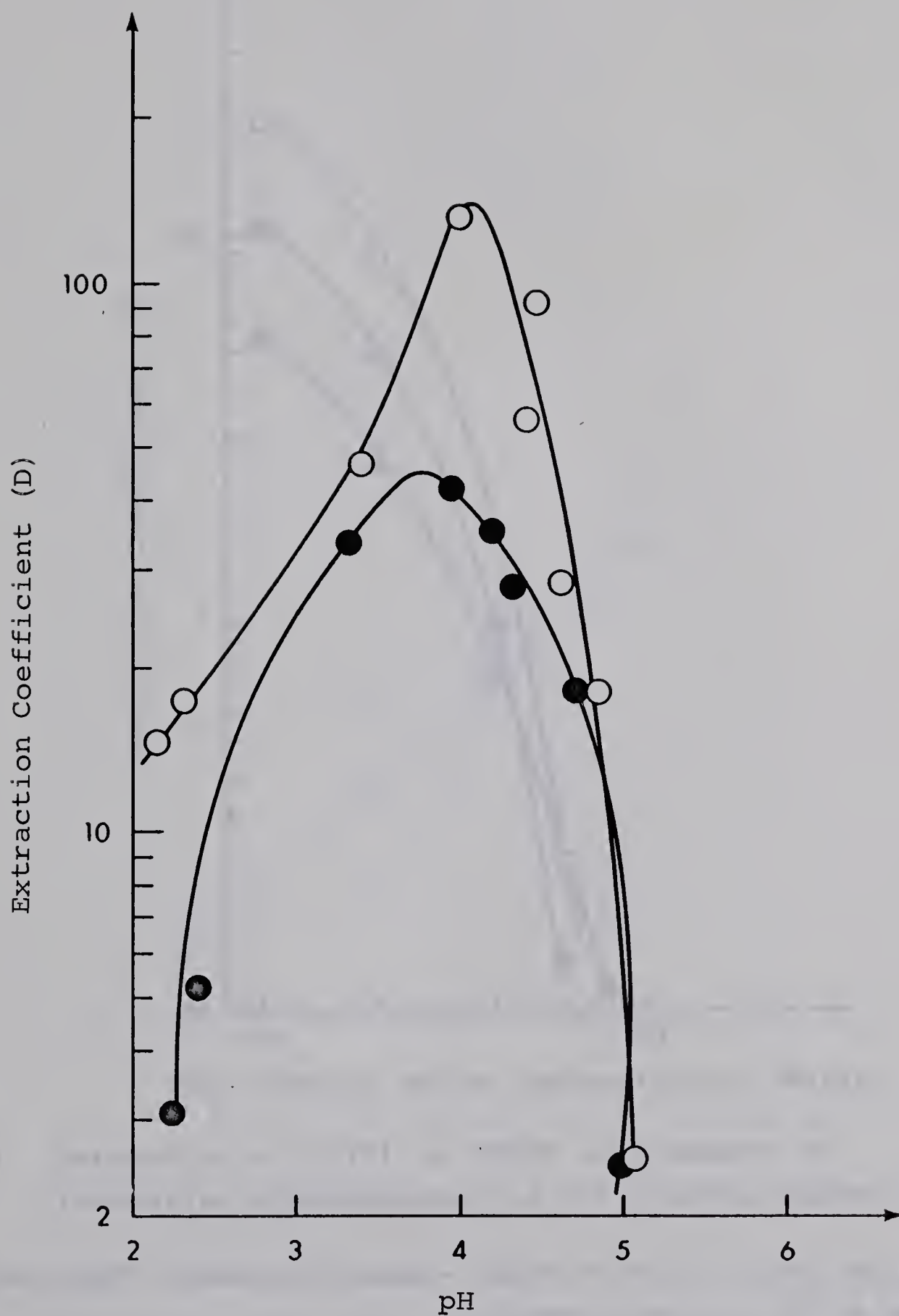


Fig.8. Extraction of V(IV) by DEHPA from acetate buffers. Closed circle, DEHPA concentration 0.01 Molar; open circle, DEHPA concentration 0.02 Molar. V(IV) concentration 4×10^{-3} M.

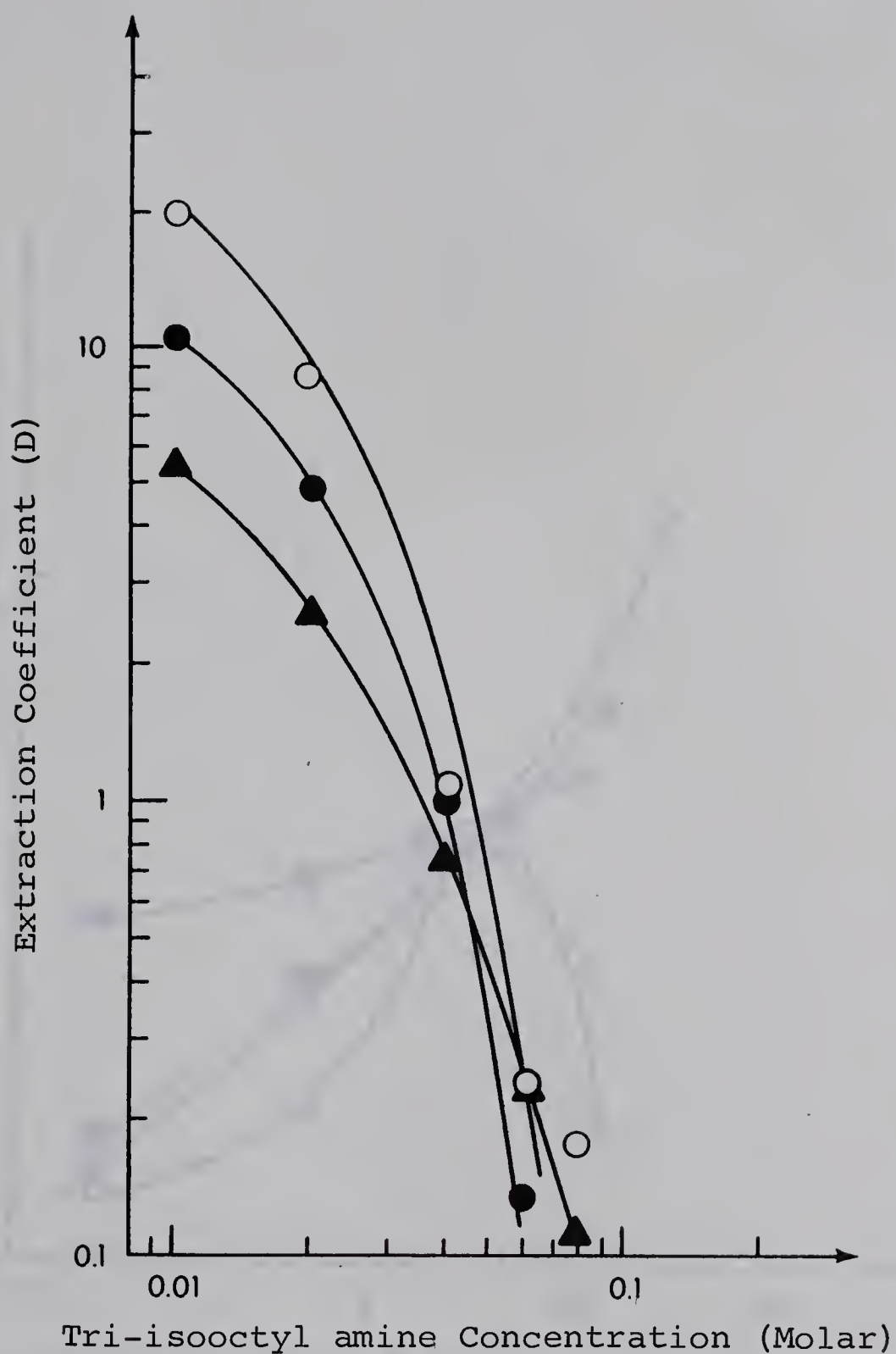


Fig.9. Extraction of V(IV) by DEHPA in presence of increasing concentration of tri-isooctyl amine.

Initial V(IV) Concentrations:- Open circle - 0.901 mg/l
 Closed circle - 225.4 mg/l
 triangle - 450.8 mg/l

pH 2.2 ± 0.1 ; DEHPA concentration 0.1 Molar.

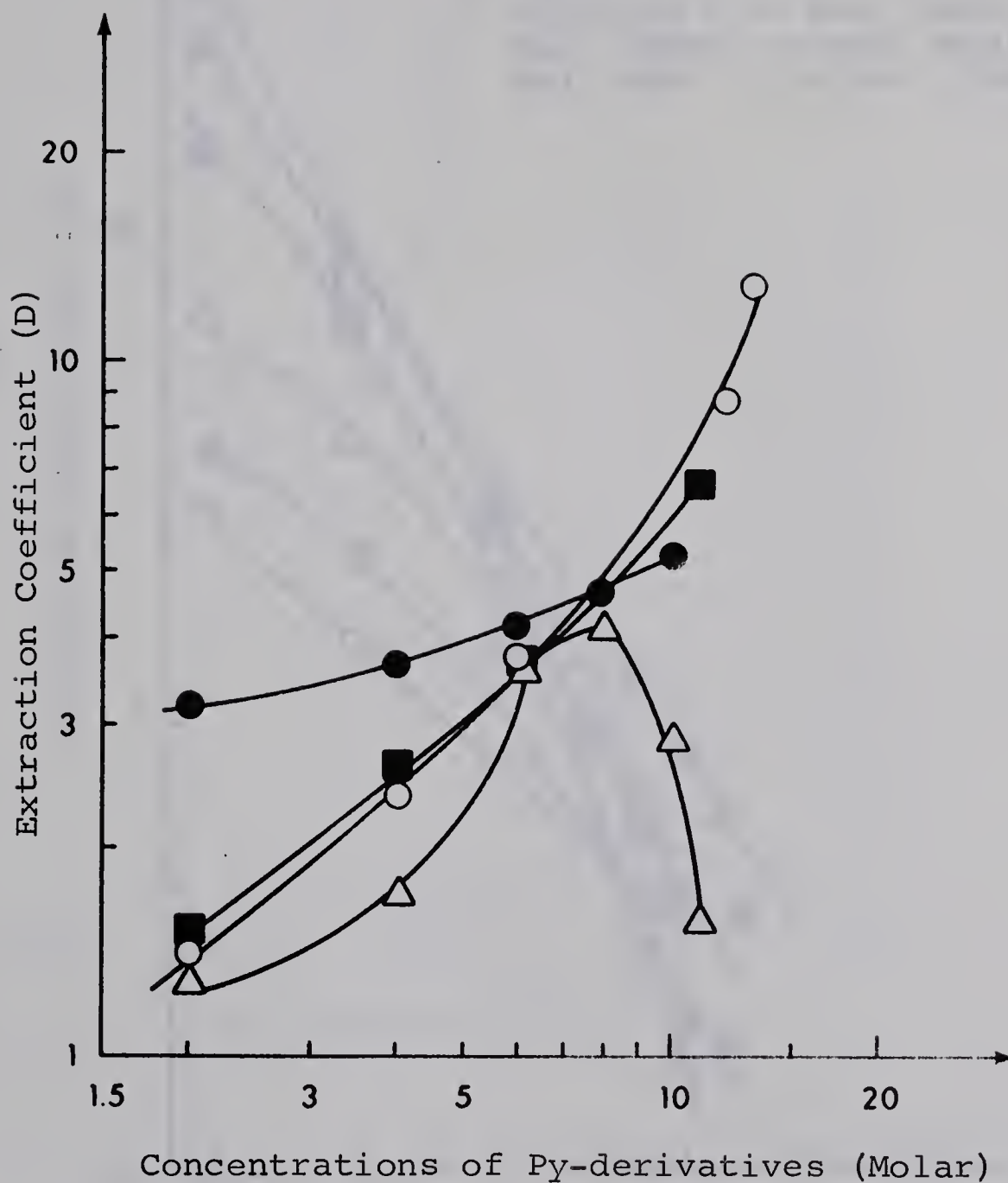


Fig.10. Variation of the extraction of V(IV) by DEHPA with the concentration of pyridine derivatives in the organic phase. Closed circle, 2-(5 nonyl) pyridine; open circle 4EP; open triangle 4IPP; closed square 2BP. DEHPA concentration 0.05 Molar.

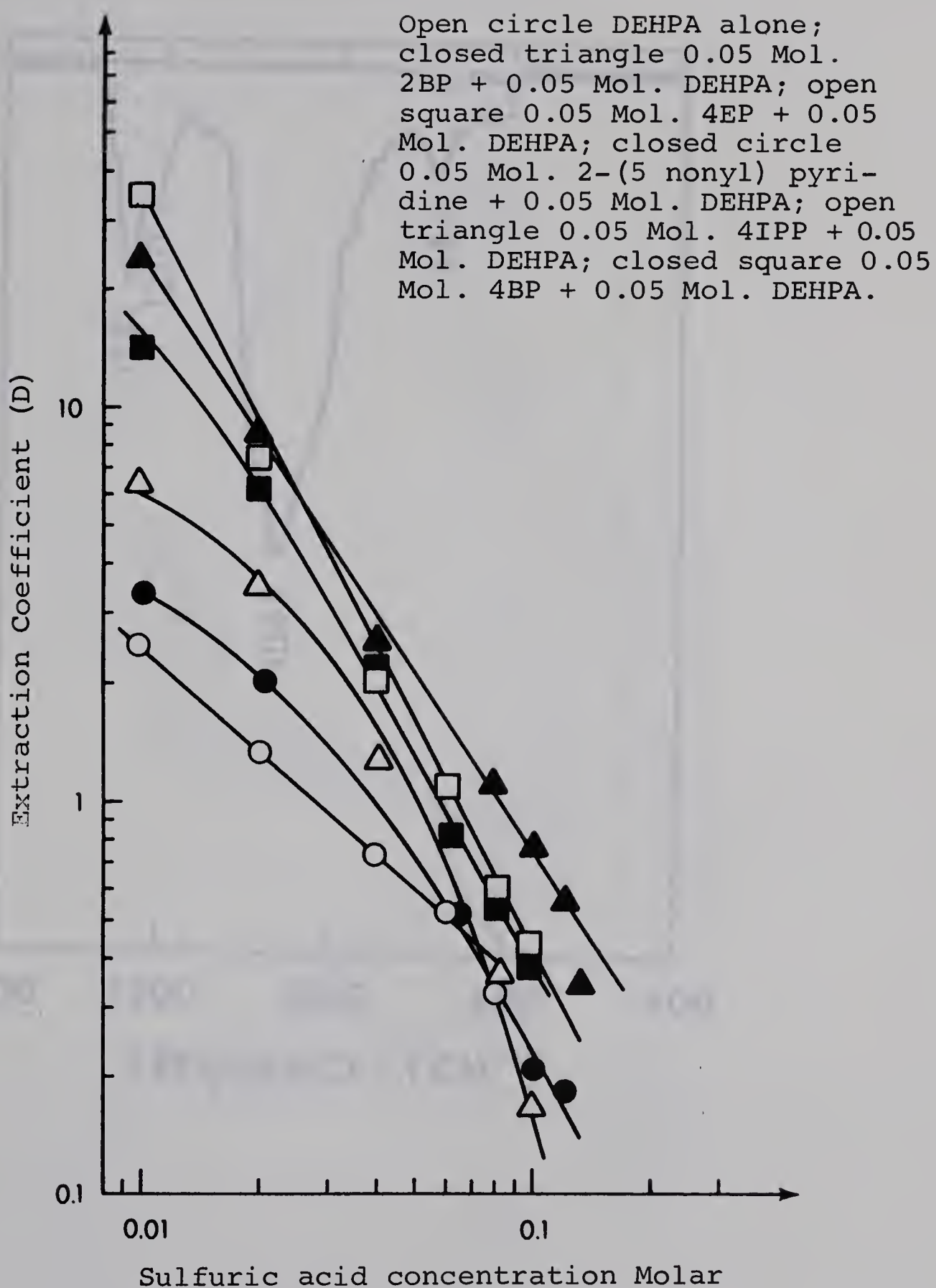
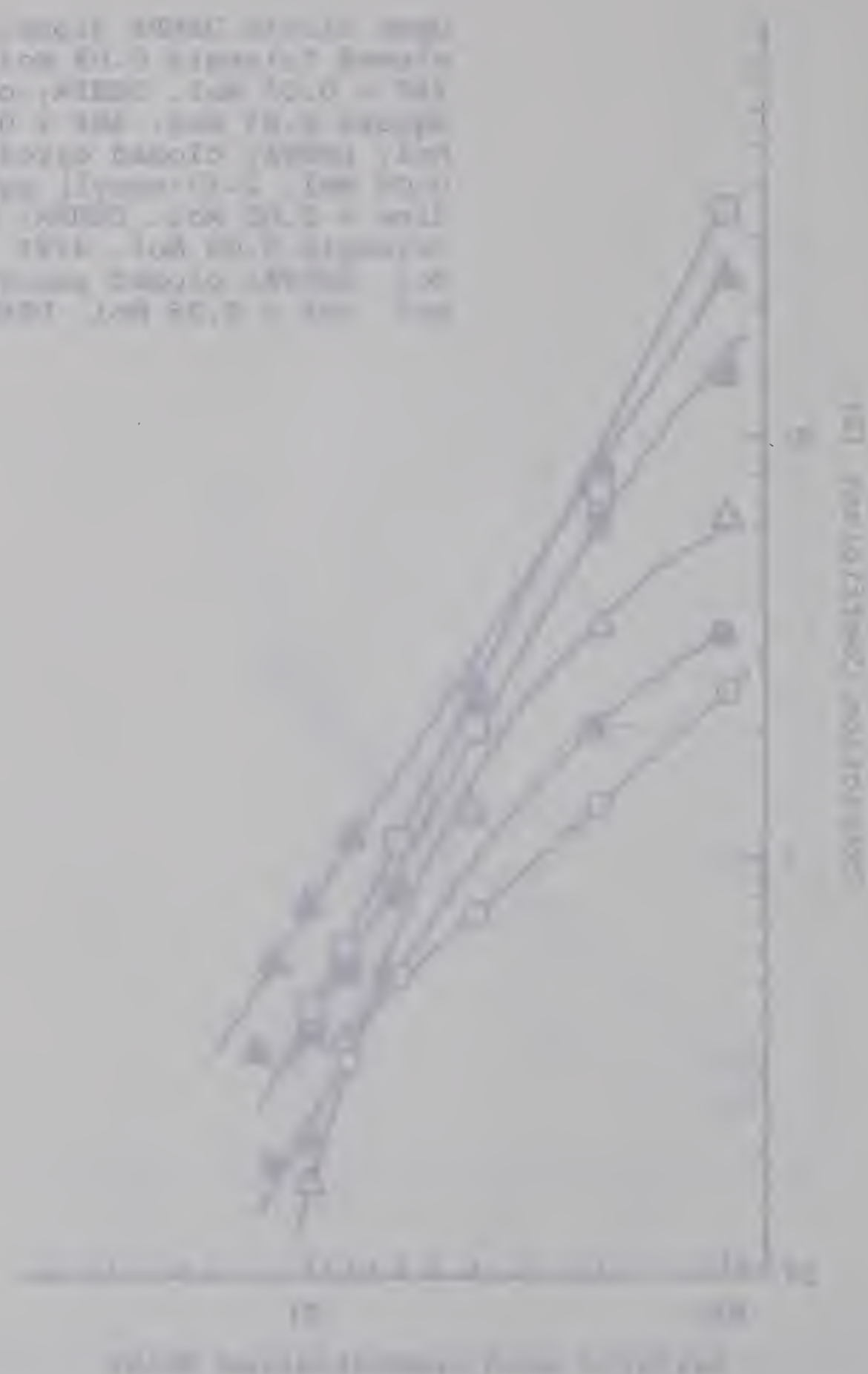


Fig.11. Dependence of the extraction of V(IV) from H_2SO_4 acid solutions by a mixture of DEHPA and pyridine derivatives.

TABLE 1. Results of the
 tests of the effect of the
 concentration of the
 solution on the rate of
 the reaction. The
 temperature was 25°C.
 The concentration of the
 solution was 0.1M.
 The concentration of the
 solution was 0.1M.
 The concentration of the
 solution was 0.1M.
 The concentration of the
 solution was 0.1M.



The results of the tests show that the rate of the reaction increases with the concentration of the solution. The rate of the reaction is highest when the concentration of the solution is 1.0M and lowest when the concentration of the solution is 0.1M.

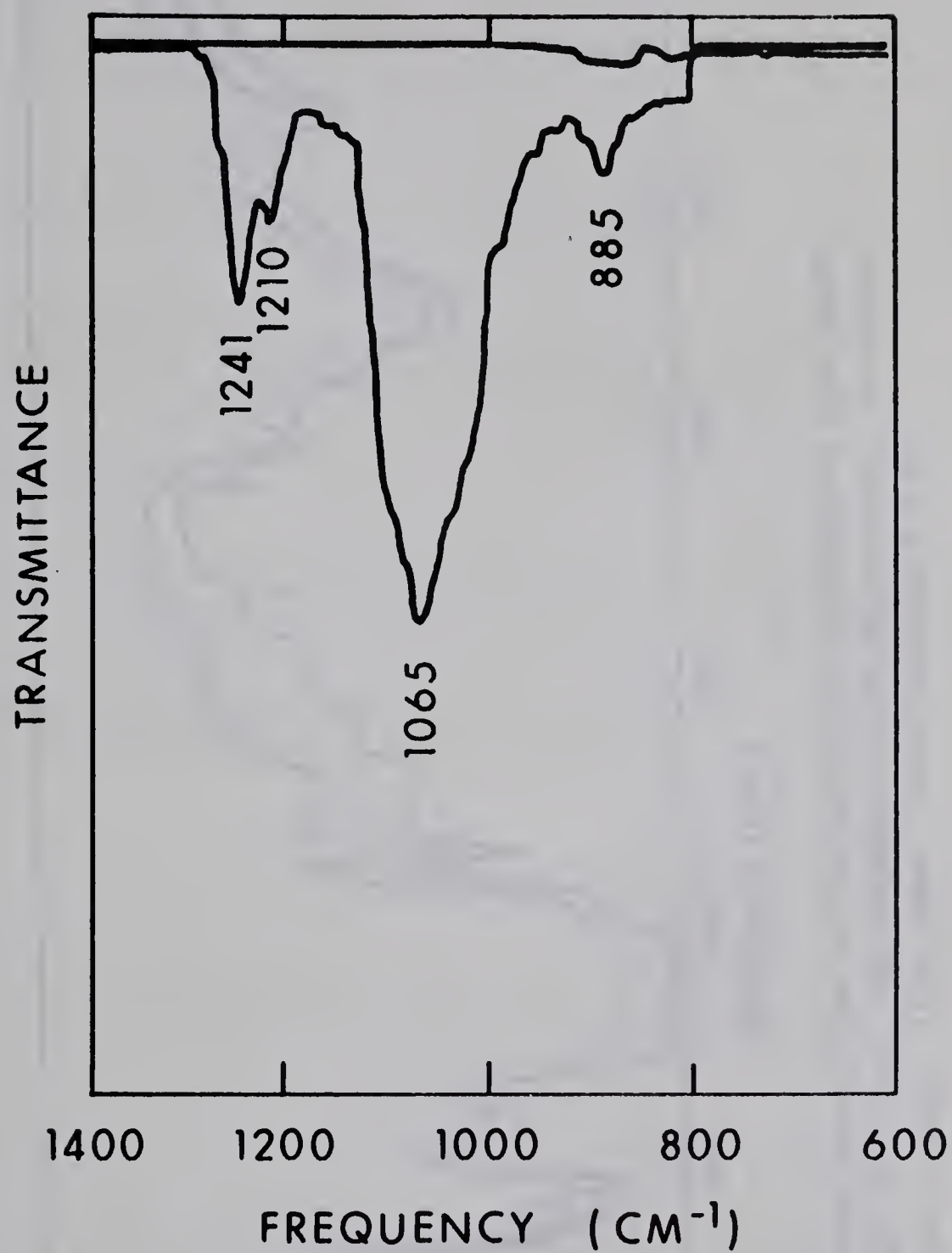


Fig. 12. IR spectrum of VDEHPA (1.25%) in benzene vs benzene. Cell thickness 0.2 mm.

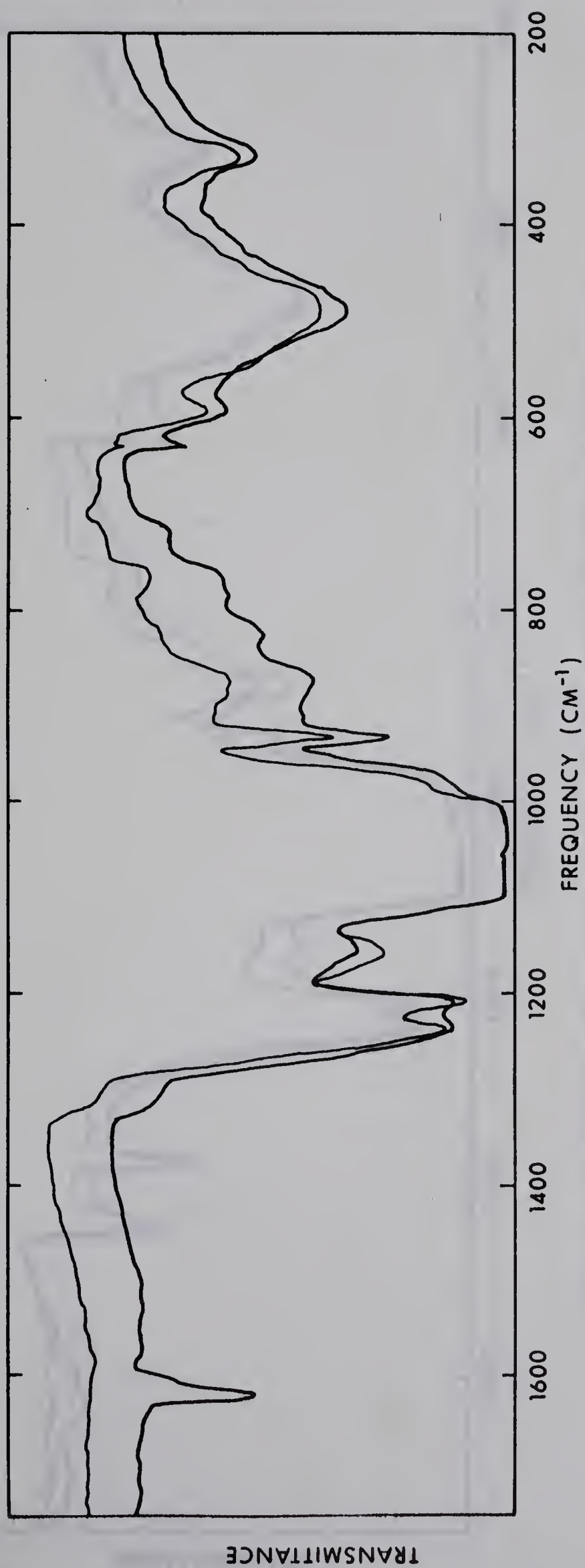


Fig. 13. IR Spectrum (heavy line) of the mixture of 0.2M 4EP and 2.5% VDEHPA in hexane vs 0.2 mol. 4EP compared with IR Spectrum of 2.5% VDEHPA in hexane vs hexane (fine line). Cell thickness 0.5 mm.

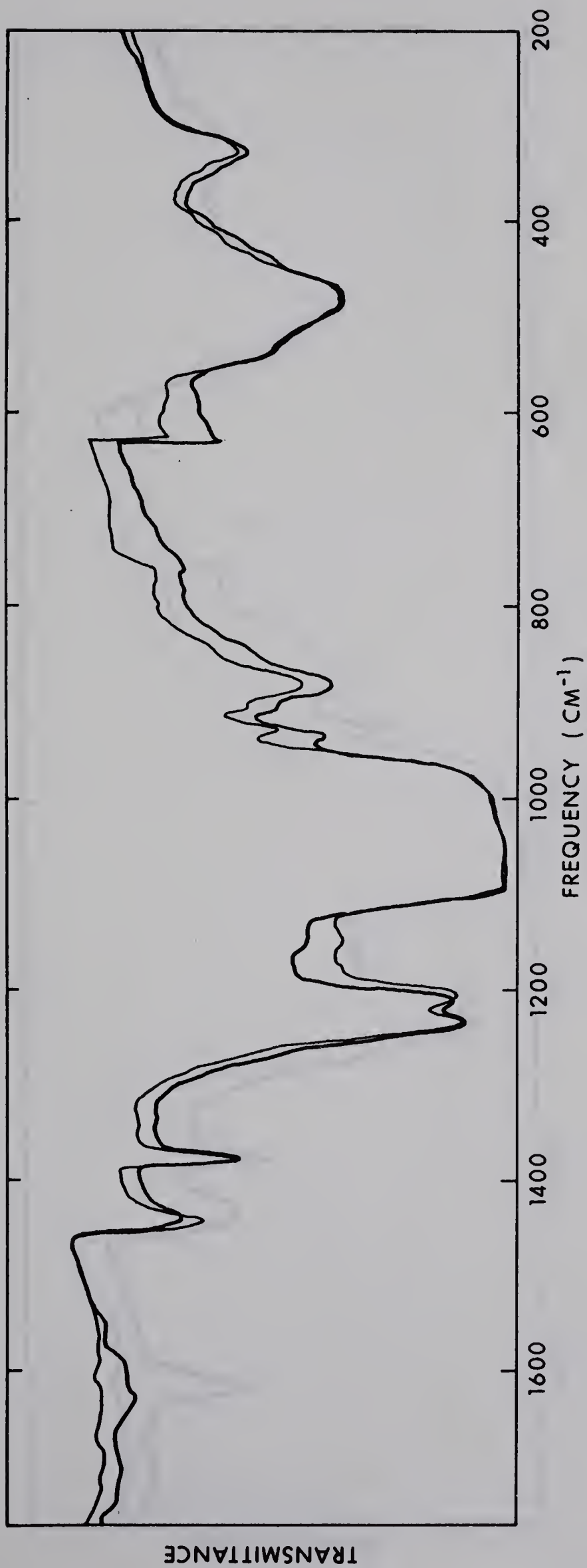


Fig. 14. IR Spectrum (heavy line) of the mixture of 0.2M 2EP and 2.5% VDEHPA in benzene vs 0.2M 2EP in benzene compared with the spectrum of 2.5% VDEHPA in benzene. . . . Cell thickness 0.5 mm.

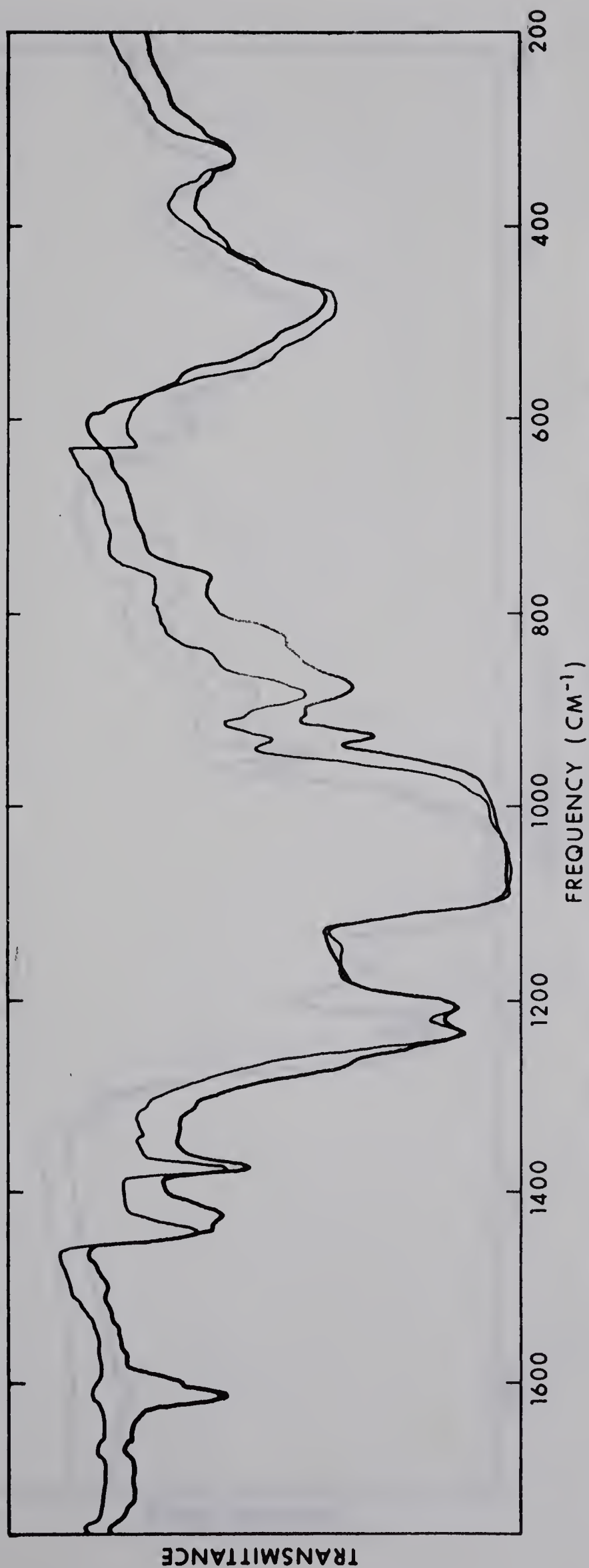


Fig. 15: IR Spectrum (heavy line) of the mixture of 0.2 mol. 4IPP and 2.5% VDEHPA in benzene vs 0.2 mol. 4IPP in benzene compared with the spectrum of 2.5% VDEHPA in benzene. Cell thickness 0.5 mm.

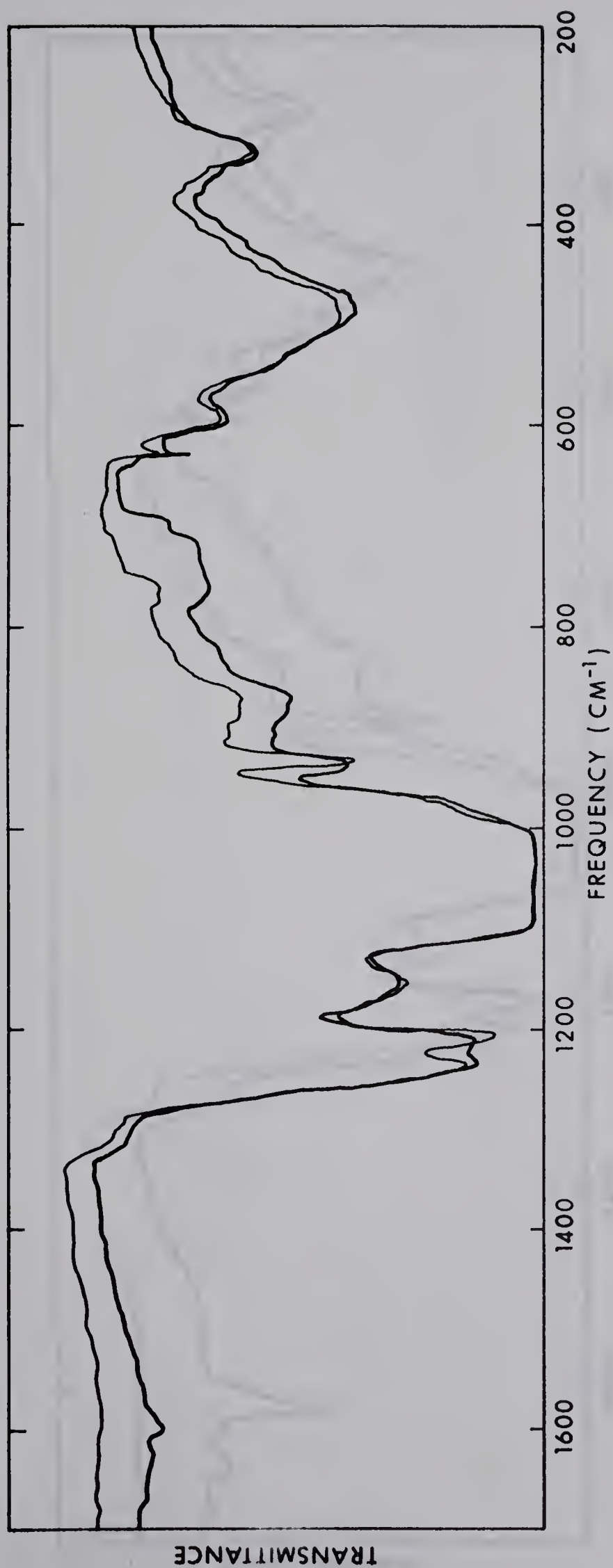


Fig. 16. IR Spectrum (heavy line) of the mixture of 0.2 mol. 2BP and 2.5% VDEHPA in hexane vs 0.2 mol. 2BP compared with spectrum of 2.5% VDEHPA alone in hexane vs hexane. Cell thickness 0.5 mm.

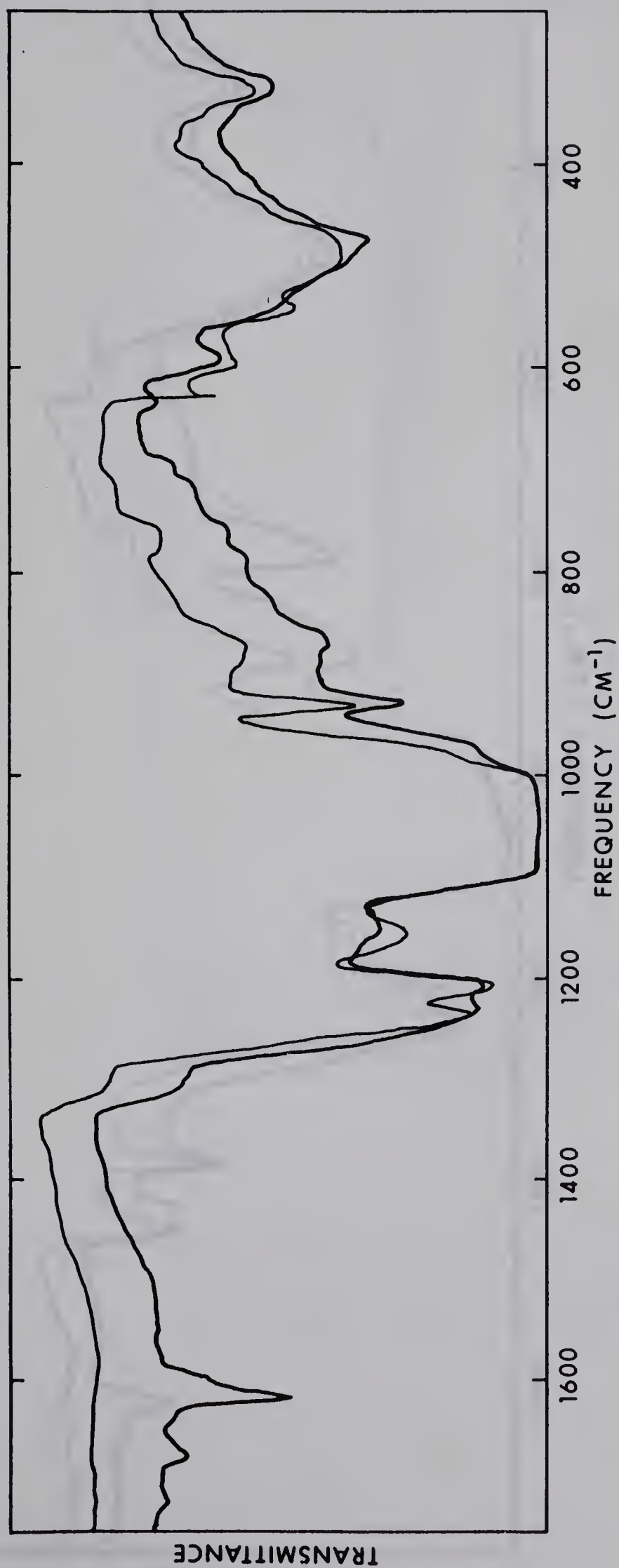


Fig. 17. IR Spectra (heavy line) of the mixture of 0.2 mol. 4BP and 2.5% VDEHPA vs 0.2M 4BP compared with the spectra (fine line) of 2.5% VDEHPA in hexane. Cell thickness 0.5 mm.

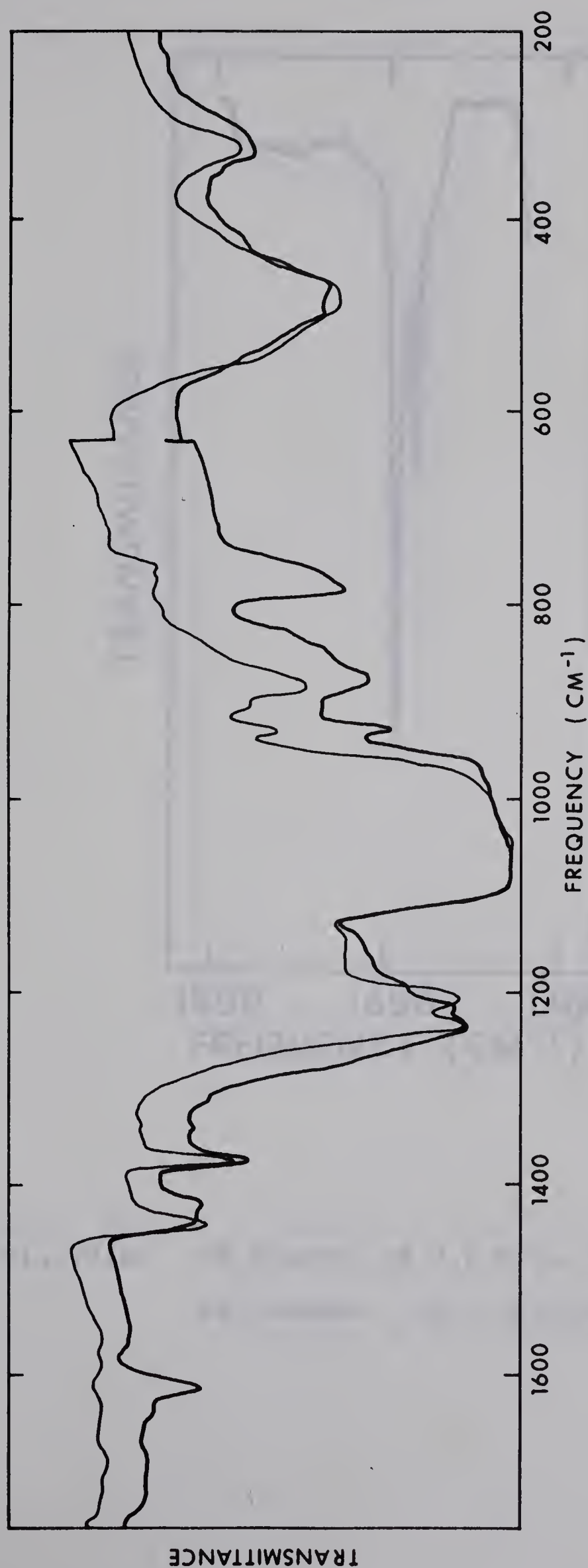


Fig. 18. IR Spectrum (heavy line) of the mixture of 0.2M β -Collidine in benzene compared with the spectrum of 2.5% VDEHPA in benzene (fine line). Cell thickness 0.5 mm.

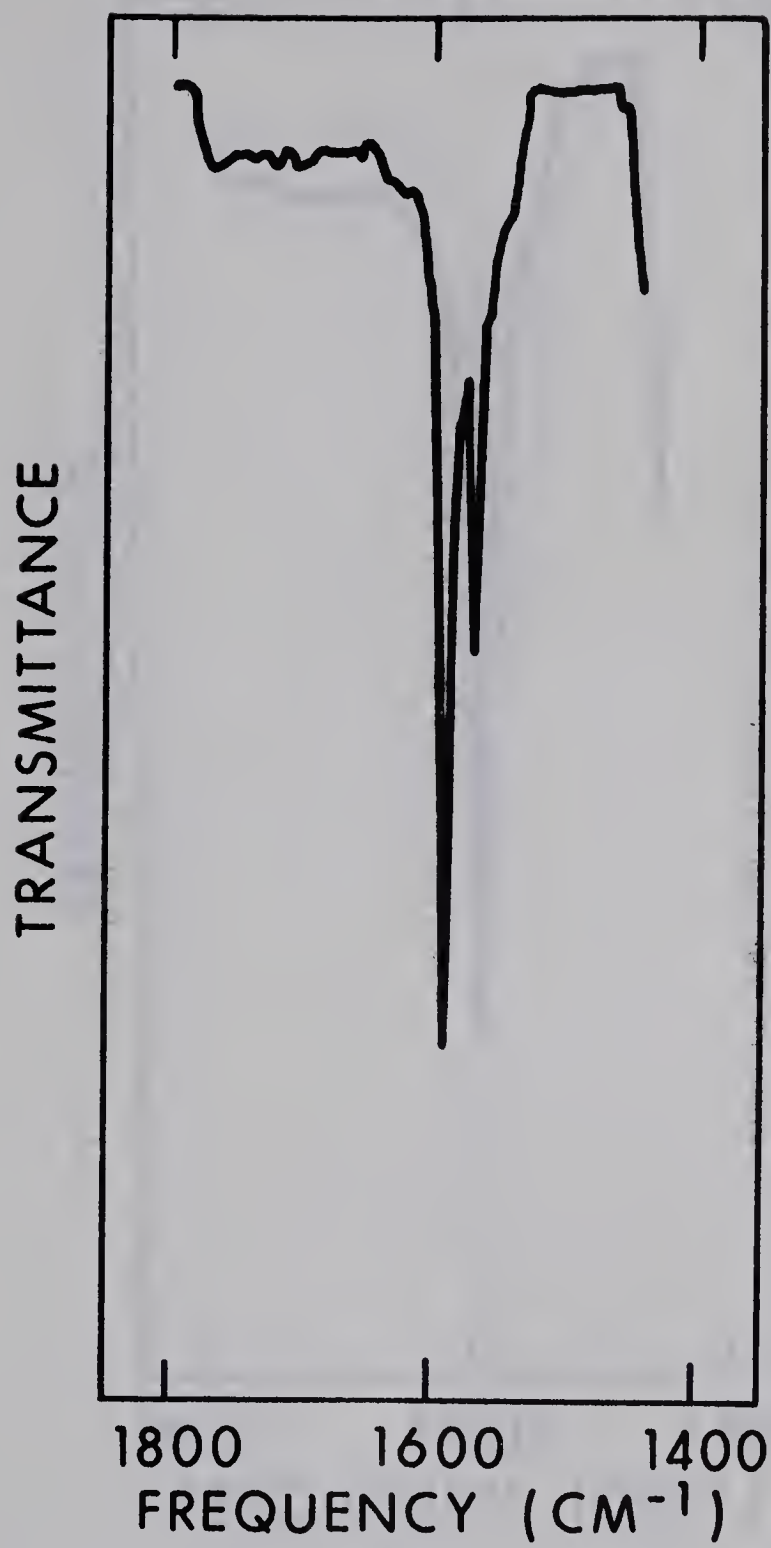


Fig.19(a) . IR spectra of 0.2 Molar 2EP in benzene
vs benzene. Cell thickness 0.2 mm.

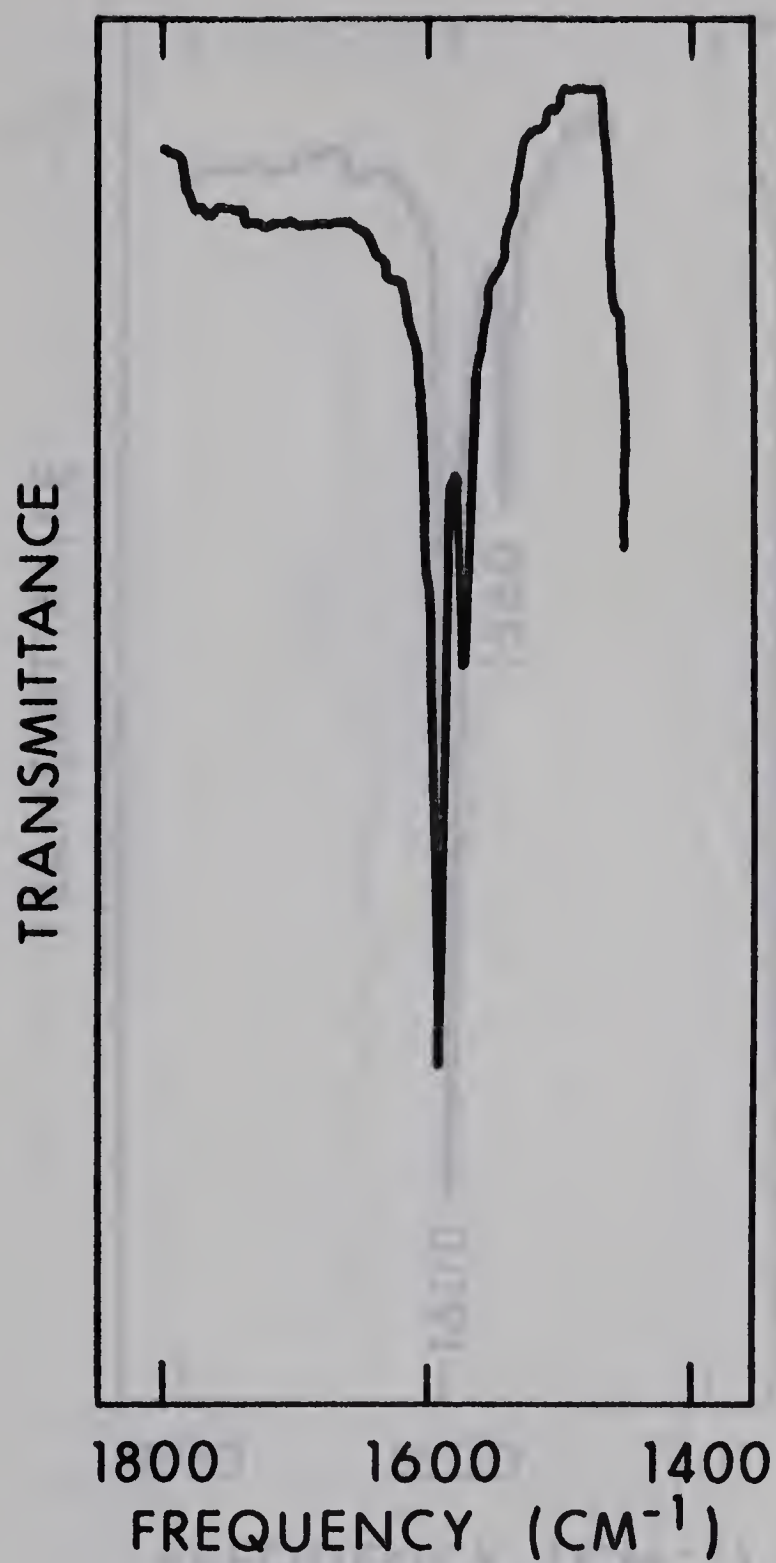


Fig. 19(b) . IR spectra of mixture of 0.2M 2EP and 2.5% VDEHPA in benzene vs benzene. Cell thickness 0.2 mm.



450 19101
 1000 19101
 1000 19101
 1000 19101

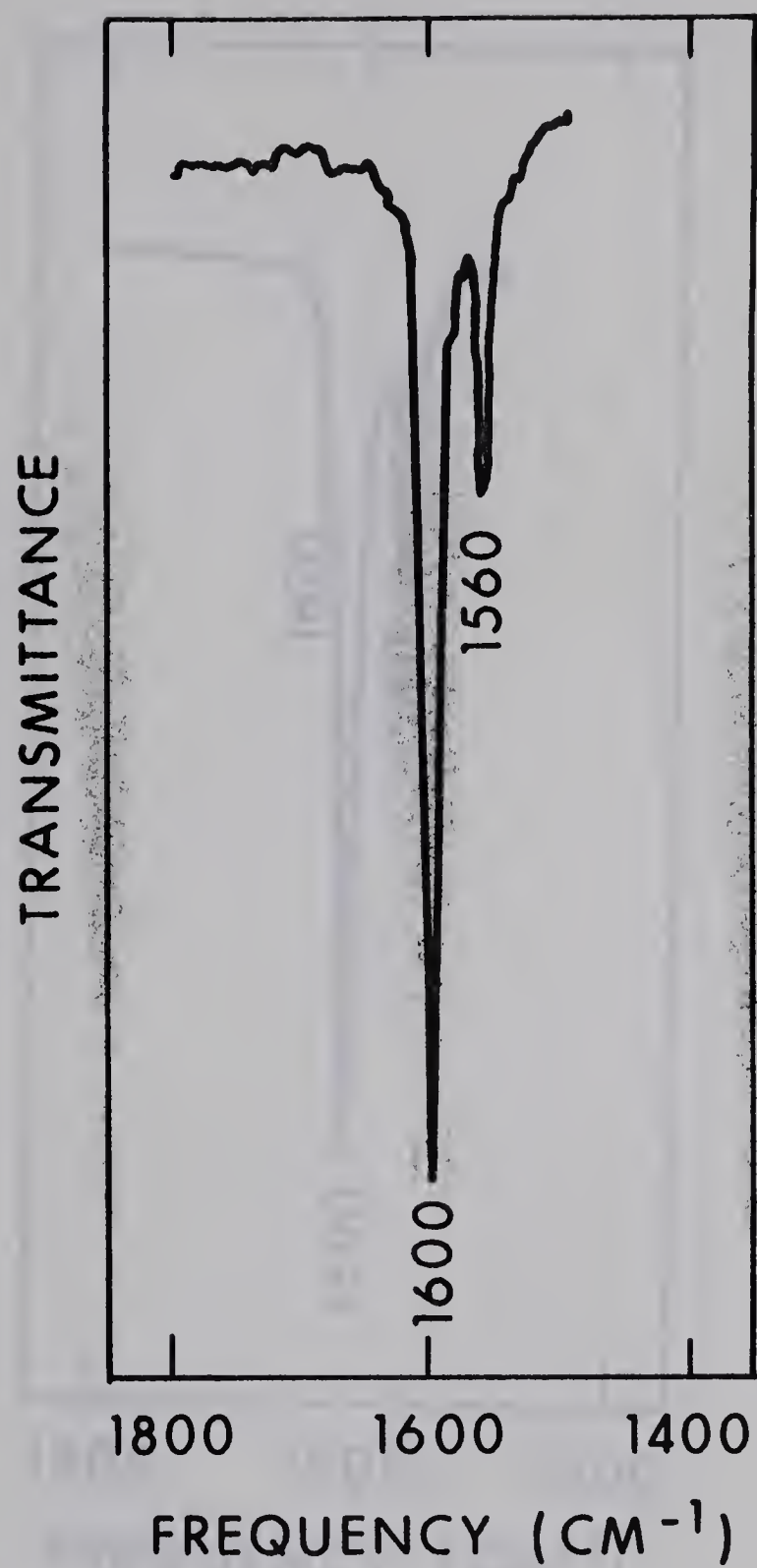


Fig. 20(a). IR spectra of 0.2M 4EP in hexane
vs hexane. Cell thickness 0.2 mm.
A portion of complete spectrum shown.

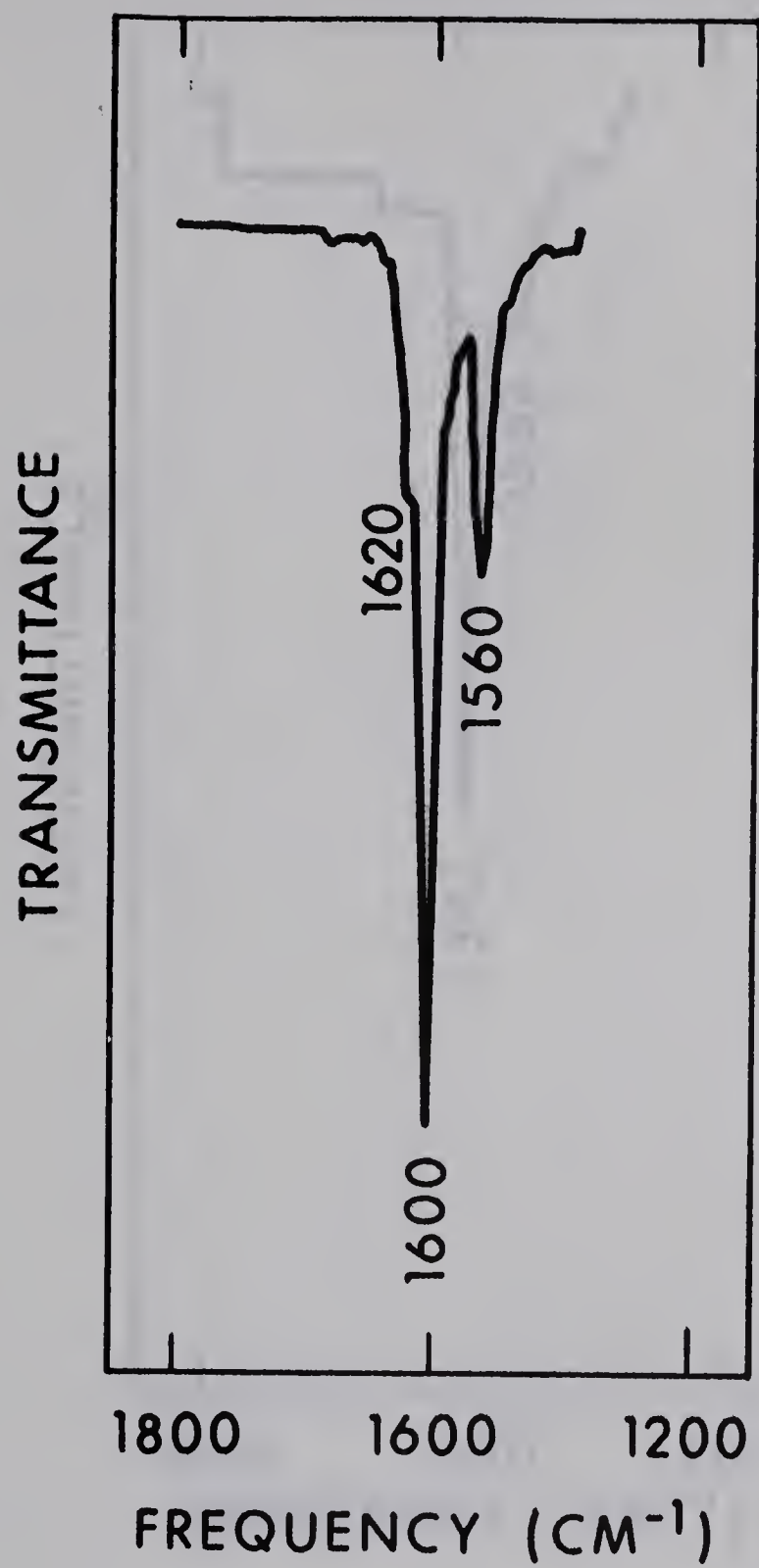


Fig.20 (b) . IR spectra of the mixture of 0.2 Mol.
4EP and 2.5% VDEHPA in hexane vs
hexane. Cell thickness 0.2 mm.

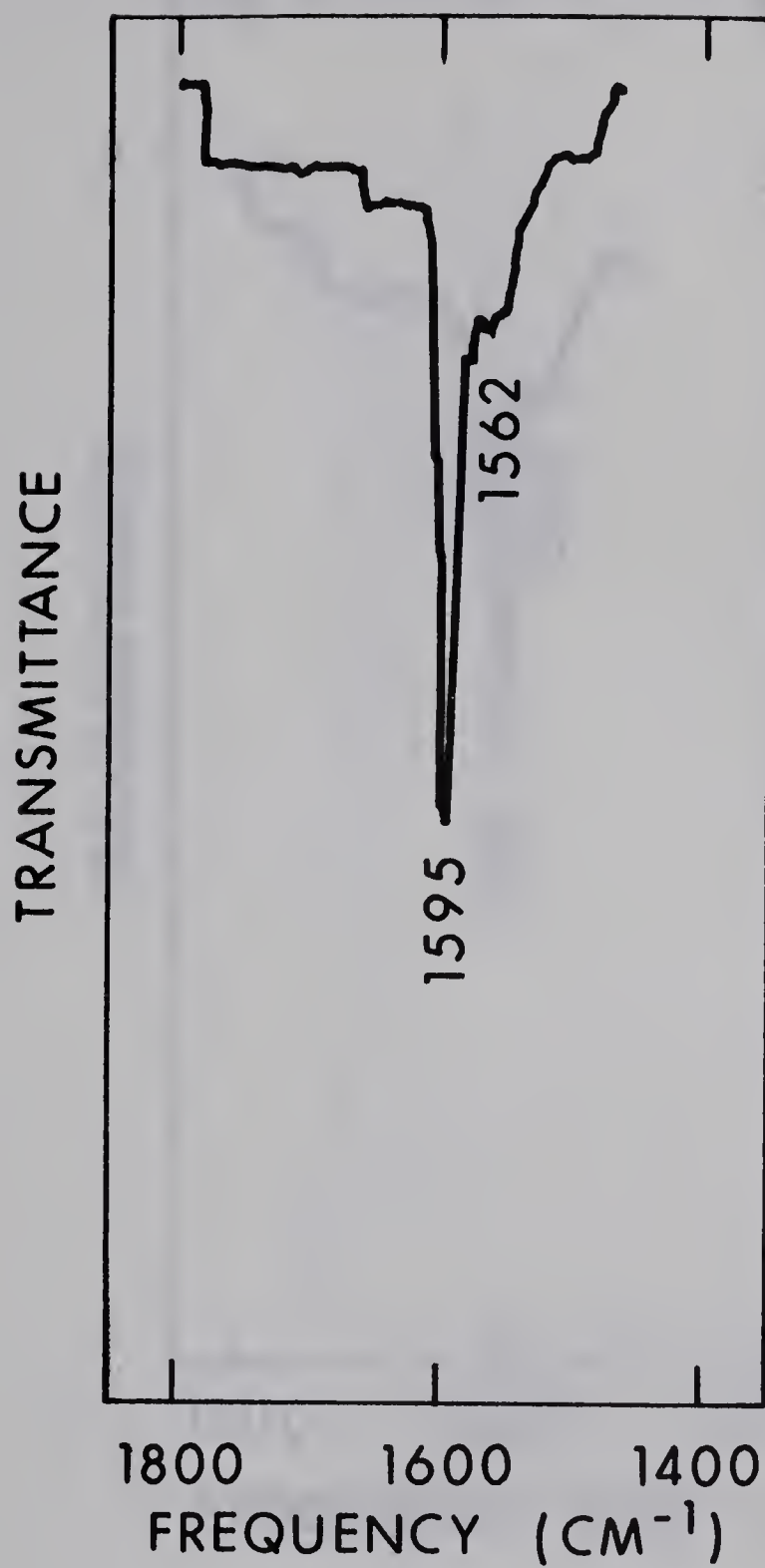


Fig.21(a) . IR spectra of 0.2 Mol. beta-Collidine in benzene vs benzene. Cell thickness 0.2mm. A portion of spectra represented.

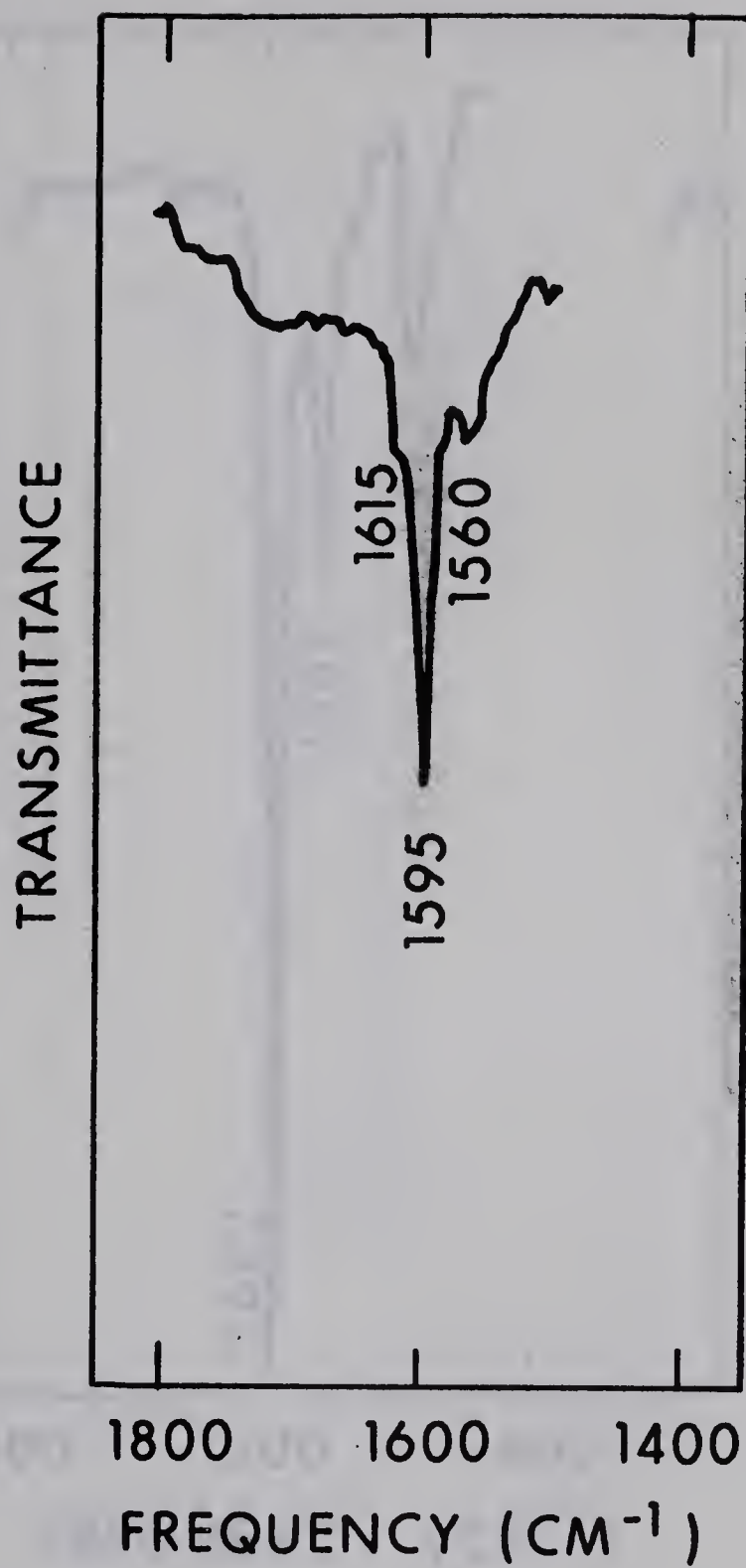


Fig.21(b) . IR spectra of a mixture of 0.2M beta-Collidine and 2.5% VDEHPA in benzene vs benzene. Cell thickness 0.2mm. A position is represented.

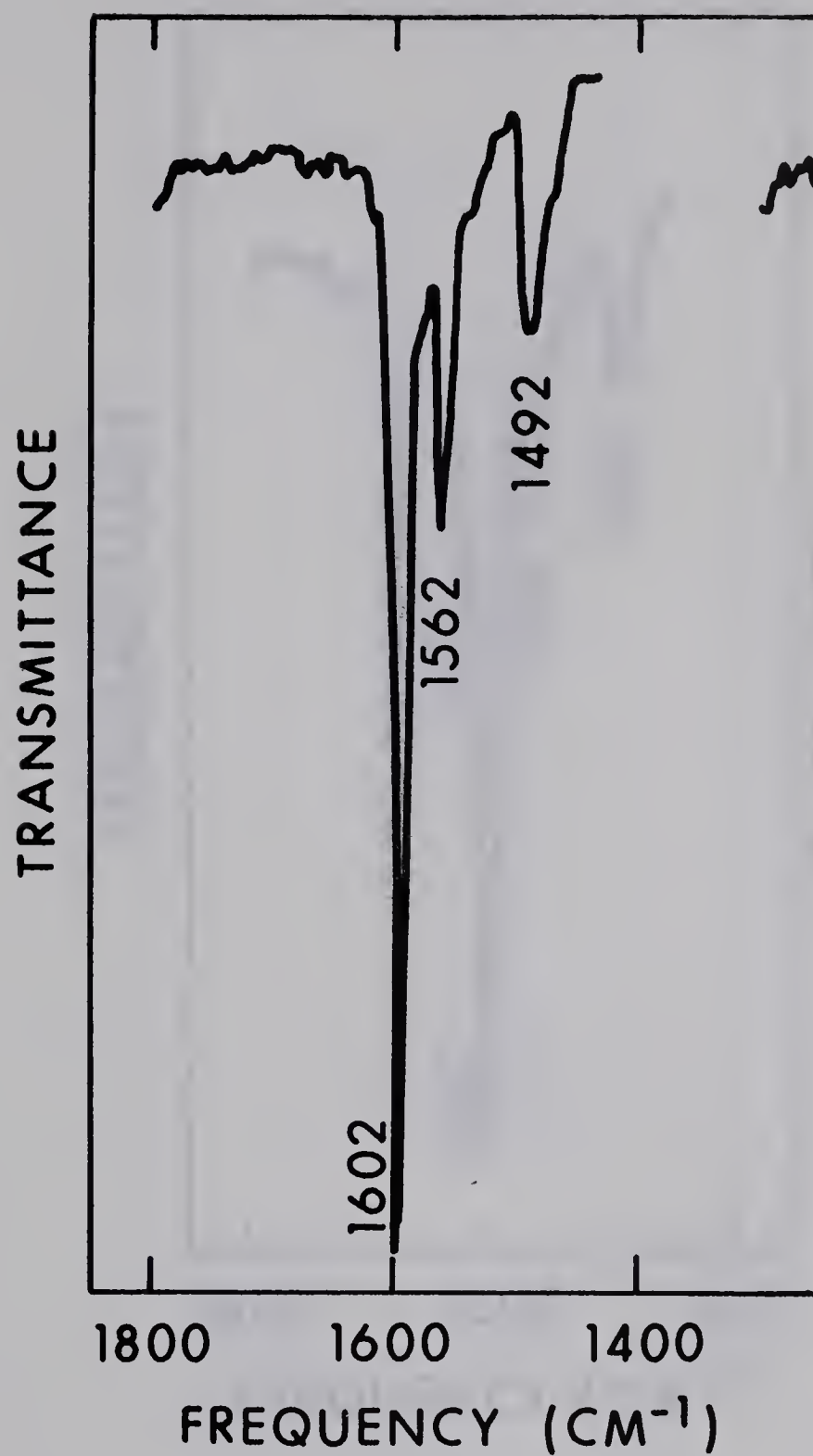


Fig.22(a) . IR spectra of 0.2M 4BP in hexane vs hexane. Cell thickness 0.2 mm. A section of complete spectrum shown.

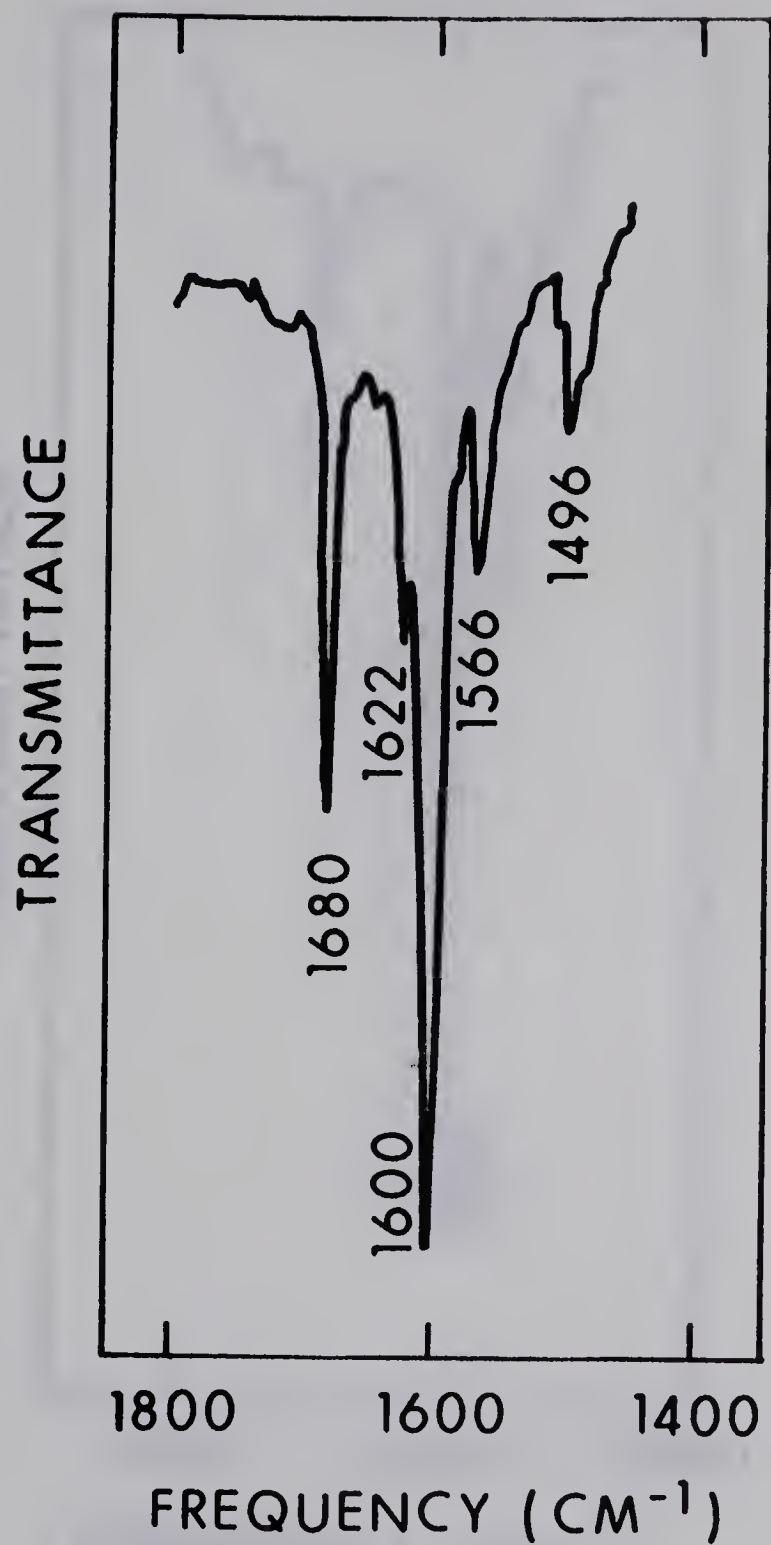


Fig.22(b) . IR spectra of the mixture 0.2M 4BP and 2.5% VDEHPA in hexane vs hexane. Cell thickness 0.2 mm. Relevant section represented.

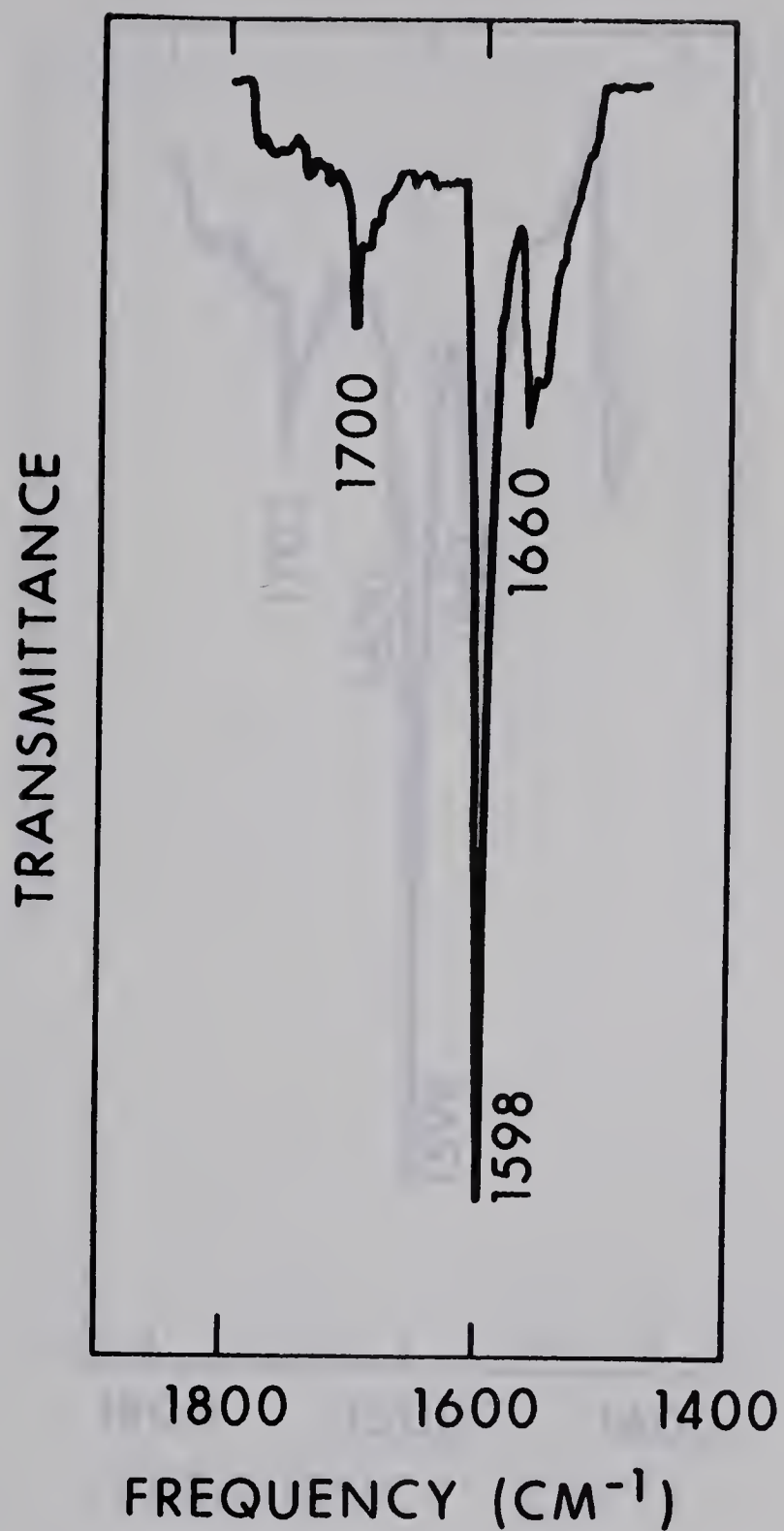


Fig.23(a). IR spectra of 0.2M 4lPP in benzene vs benzene. Cell thickness 0.2 mm. A position of complete spectrum shown.

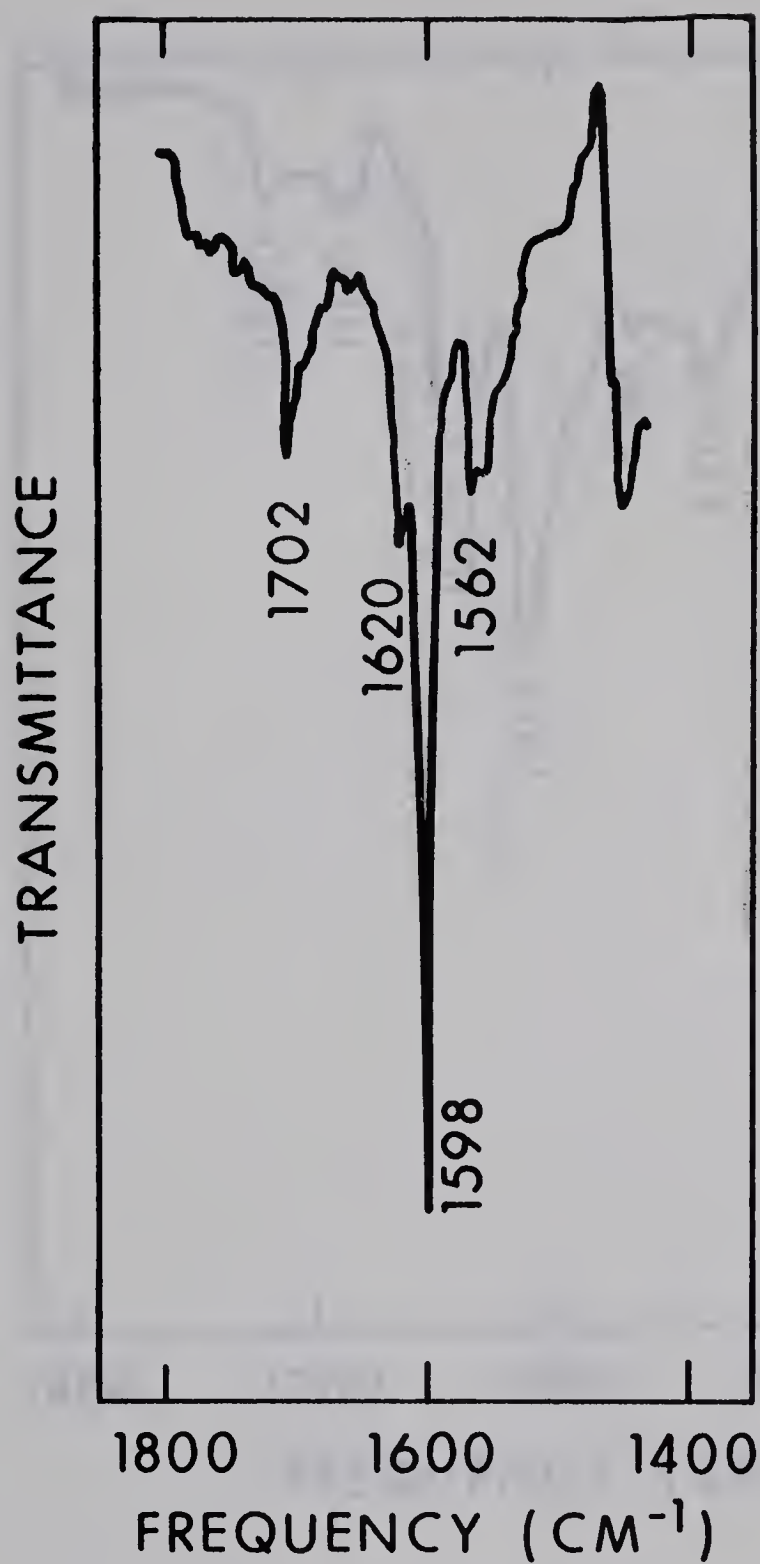


Fig.23(b) . IR spectra of a mixture of 0.2 Mol. 4IPP + 2.5% VDEHPA in benzene vs benzene. Cell thickness 0.2 mm. A section of complete spectrum.

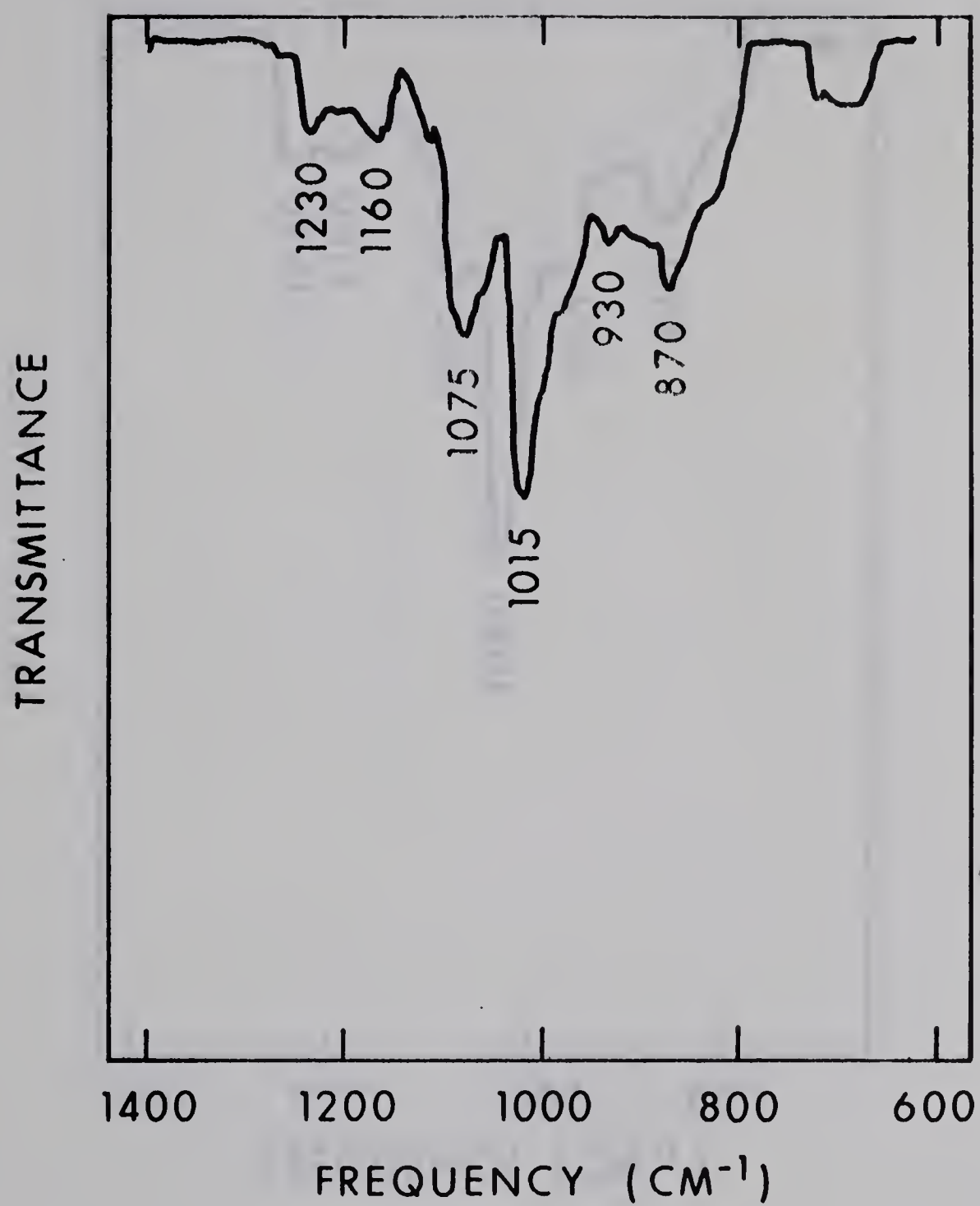


Fig. 24. IR spectra of VDEHPA 1% in 2EP vs 2EP. Cell thickness 0.2 mm.

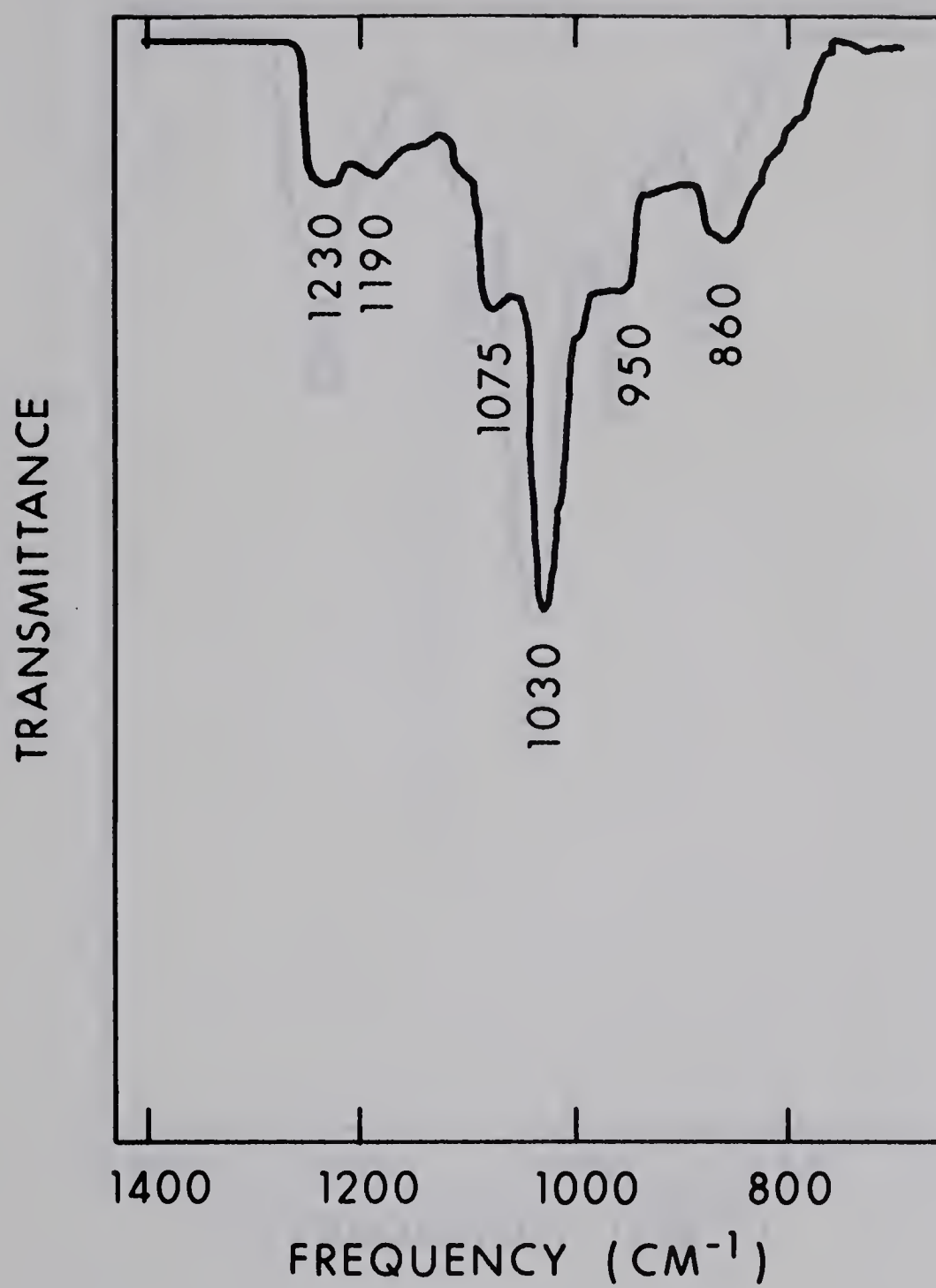


Fig. 25. IR spectra of VDEHPA (1%) in 4EP vs 4EP. Cell thickness 0.2 mm.

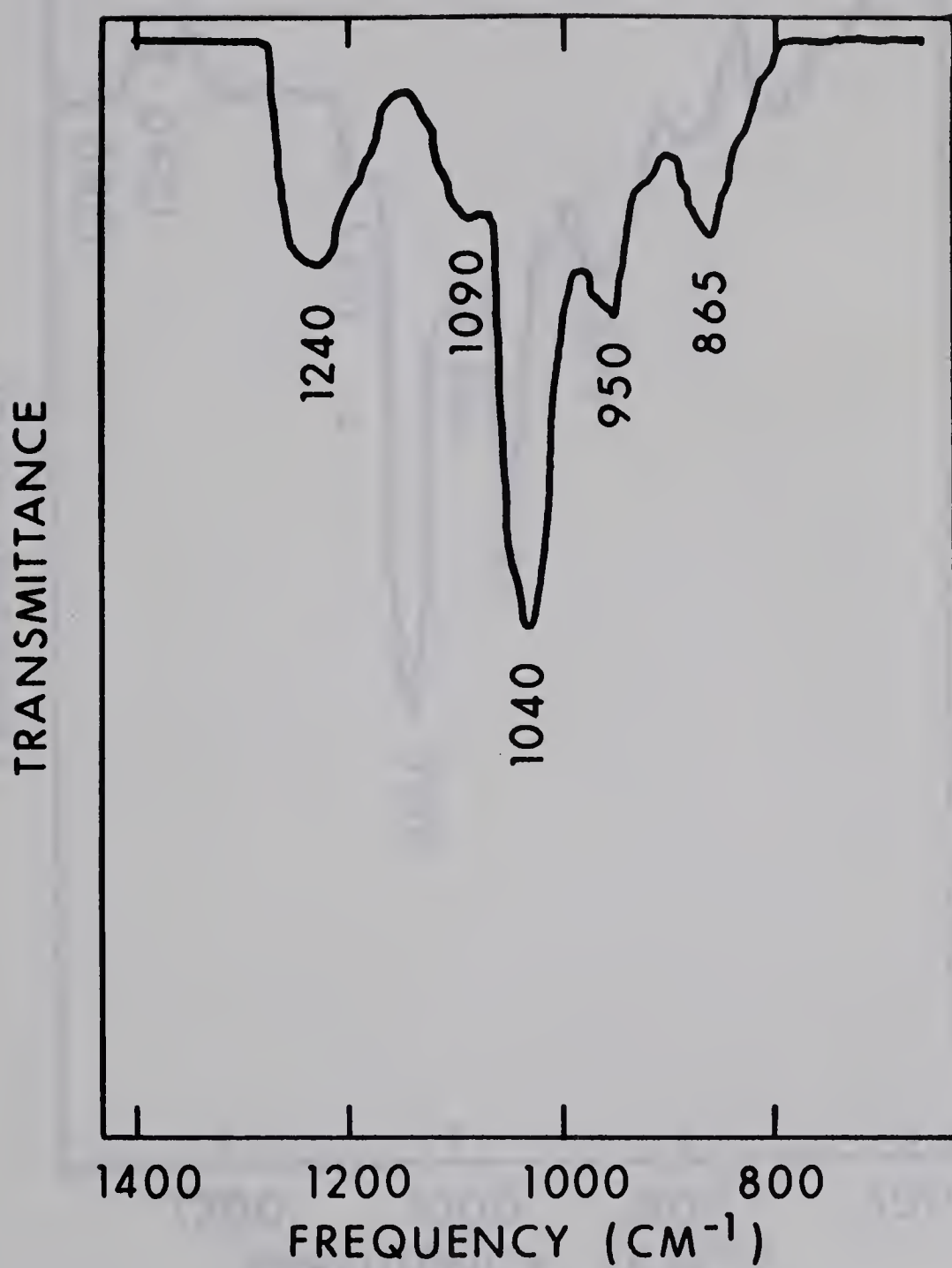


Fig. 26. IR spectra of VDEHPA 1% in 4BP vs 4BP. Cell thickness 0.2 mm.

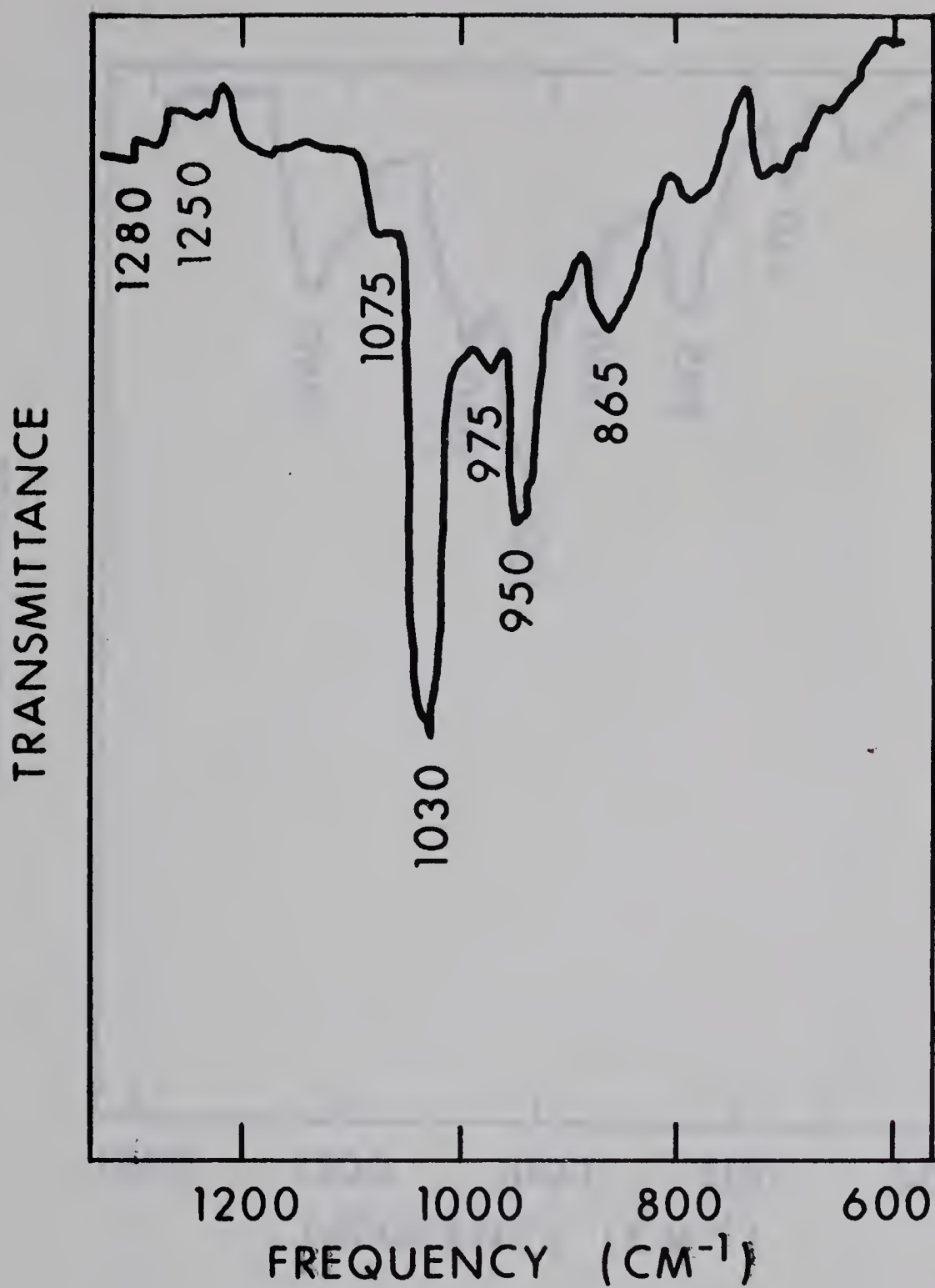


Fig.27. IR spectra of 1% VDEHPA in 4IPP
vs 4IPP.

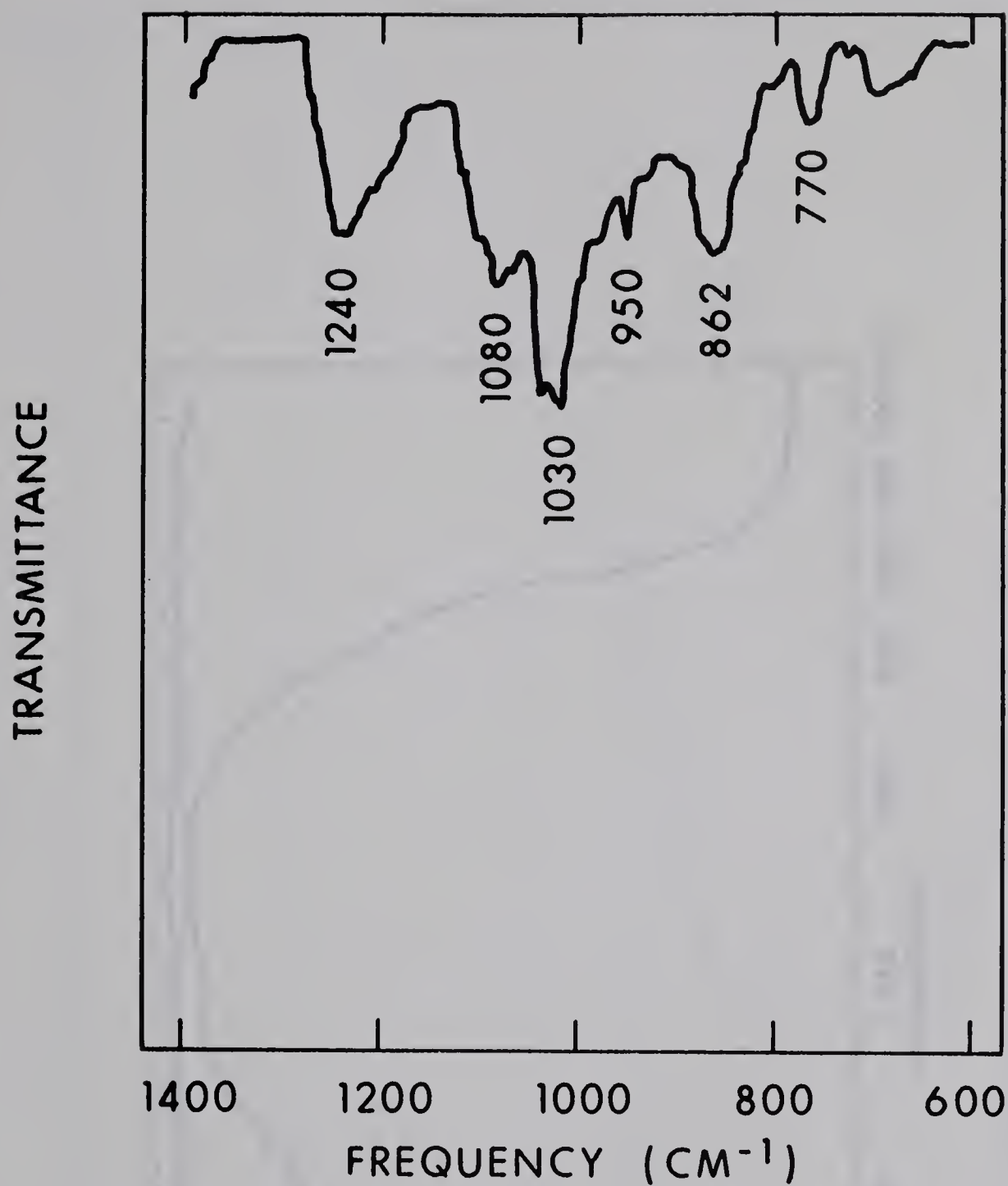


Fig. 28. IR spectra of 1% VDEHPA in beta-Collidine vs beta-Collidine. Cell thickness 0.2 mm.

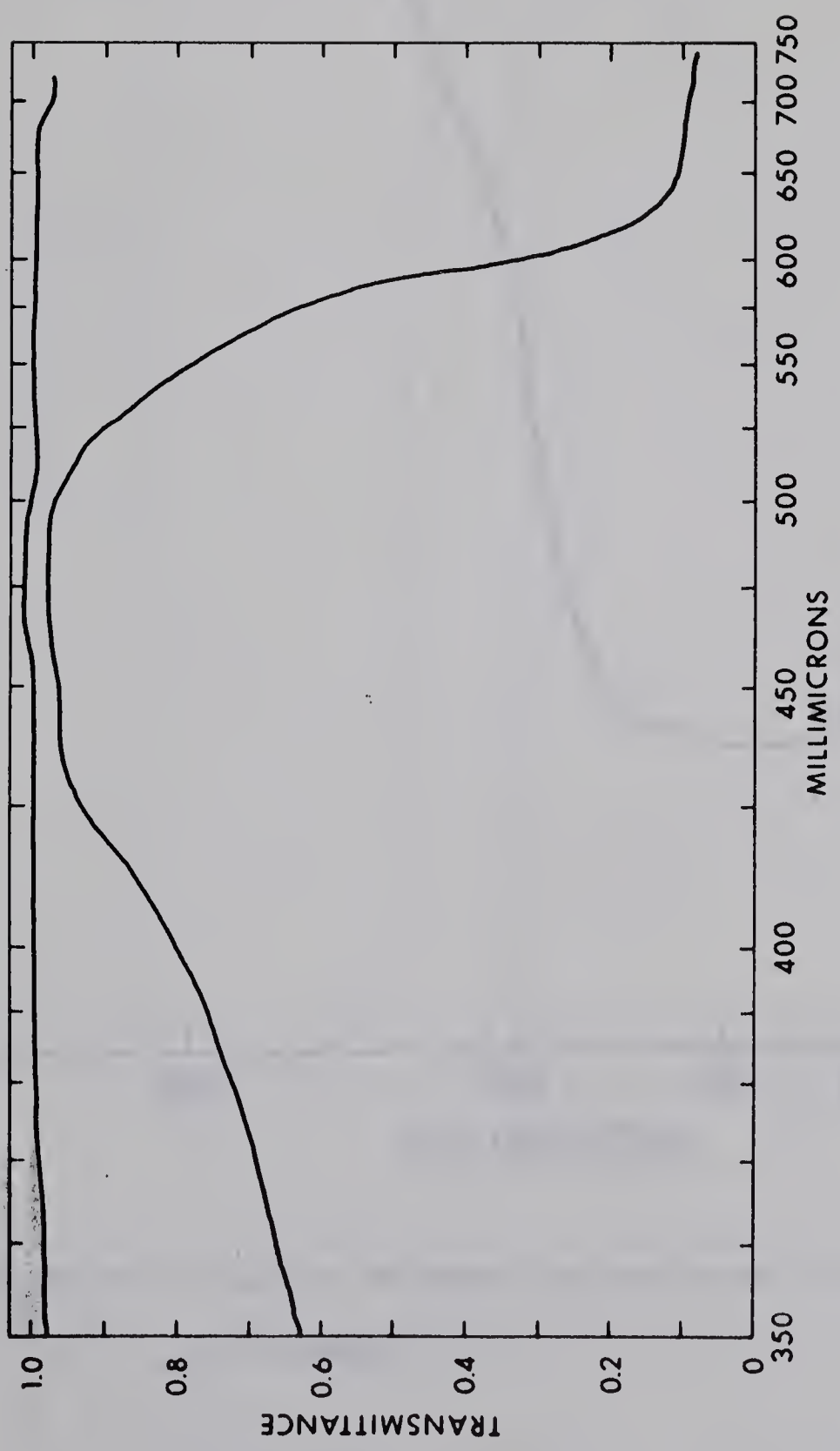


Fig.29(a) . Visible absorption spectrum of 5% VDEHPA in hexane .

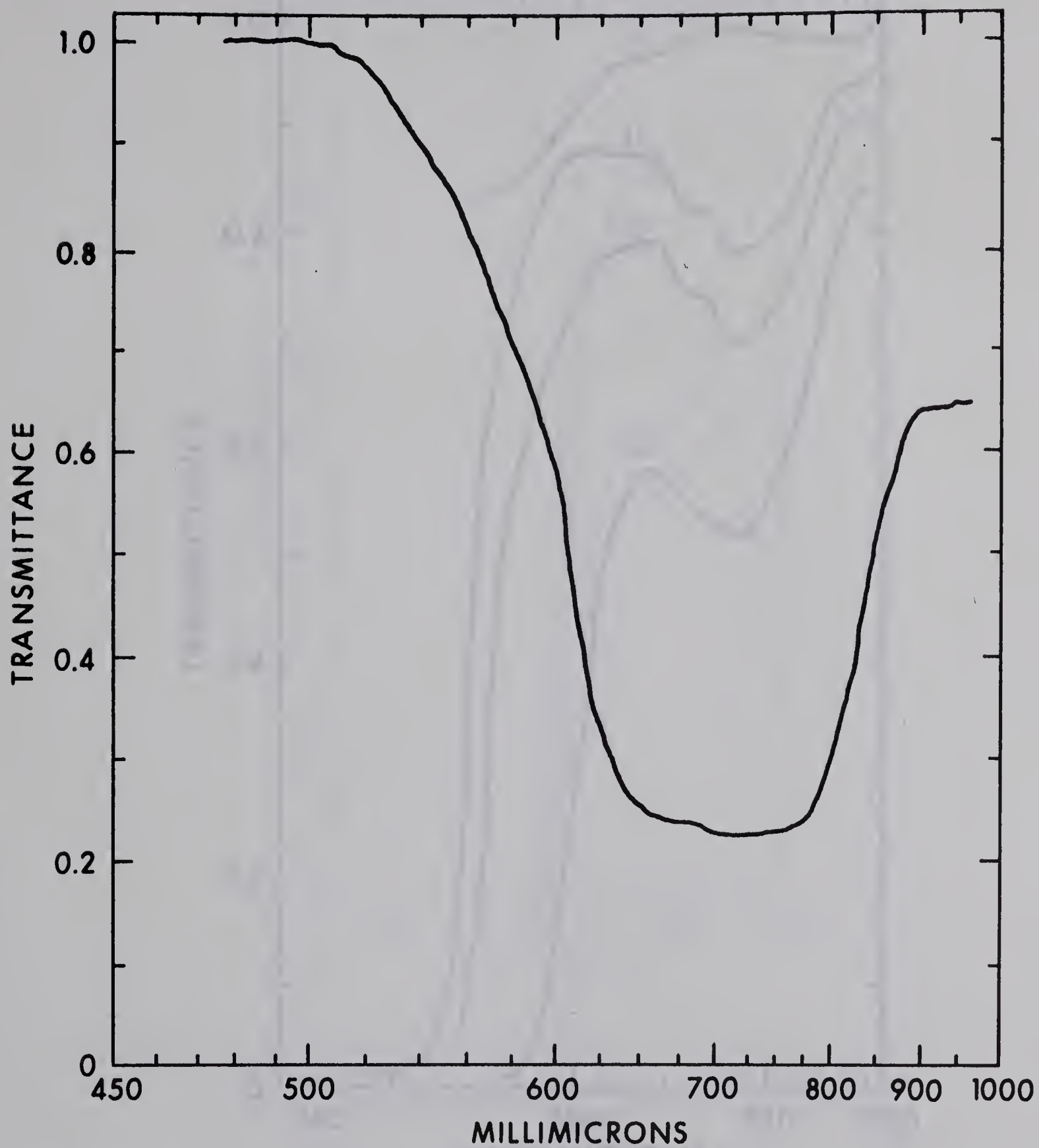


Fig.29(b) . Visible absorption spectrum of 5% VDEHPA
in hexane.

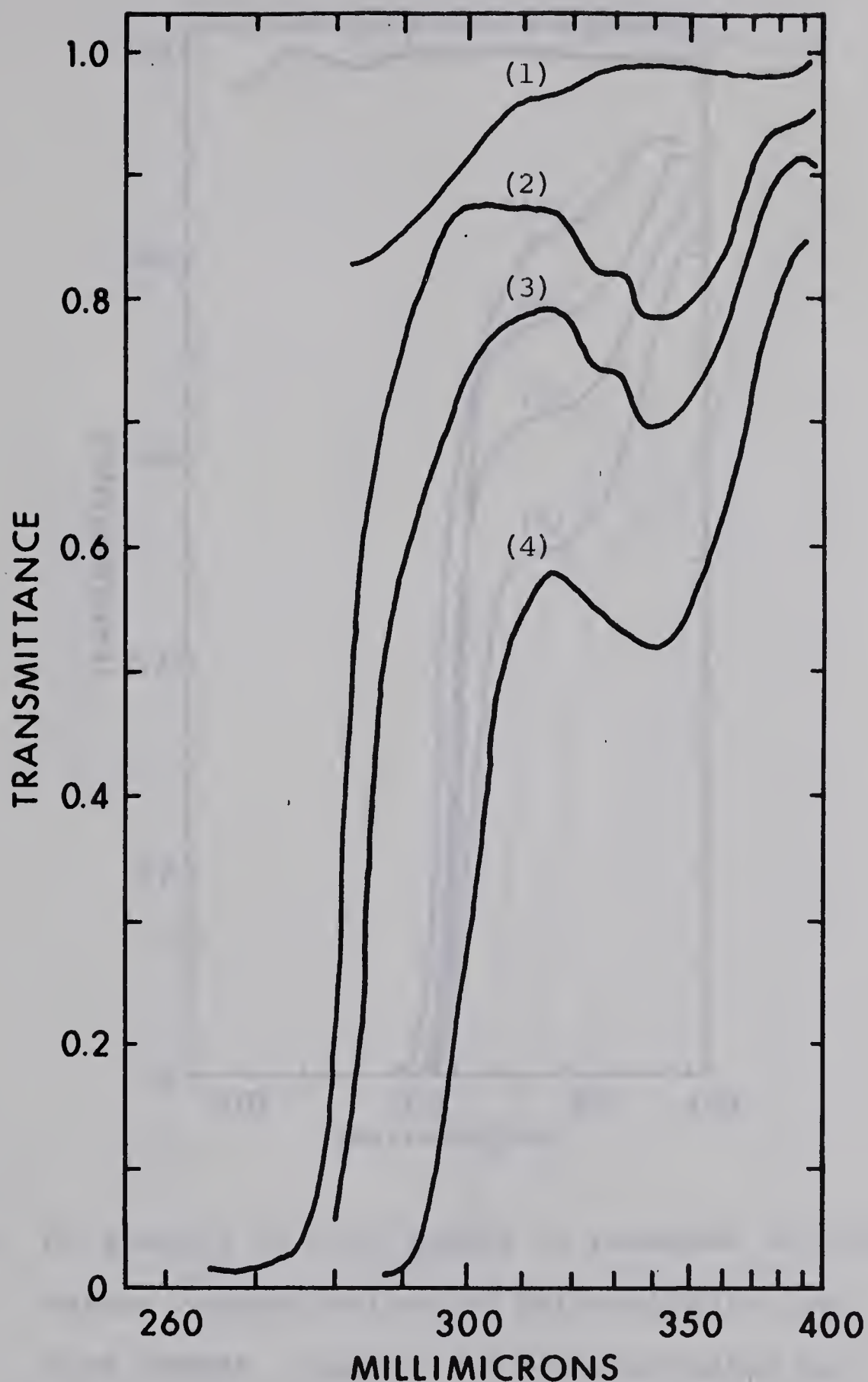


Fig.30. UV spectra of 0.5% VDEHPA in presence of different concentrations of 4-ethyl pyridine vs 0.5% VDEHPA. 4EP do not absorb in the range of wave length shown. Spectra were obtained after sufficient time for equilibrium.

(1) 0.2 Molar 4EP in benzene

(3) 0.04 Molar 4EP

(2) 0.02 Molar 4EP

(4) 0.08 Molar 4EP

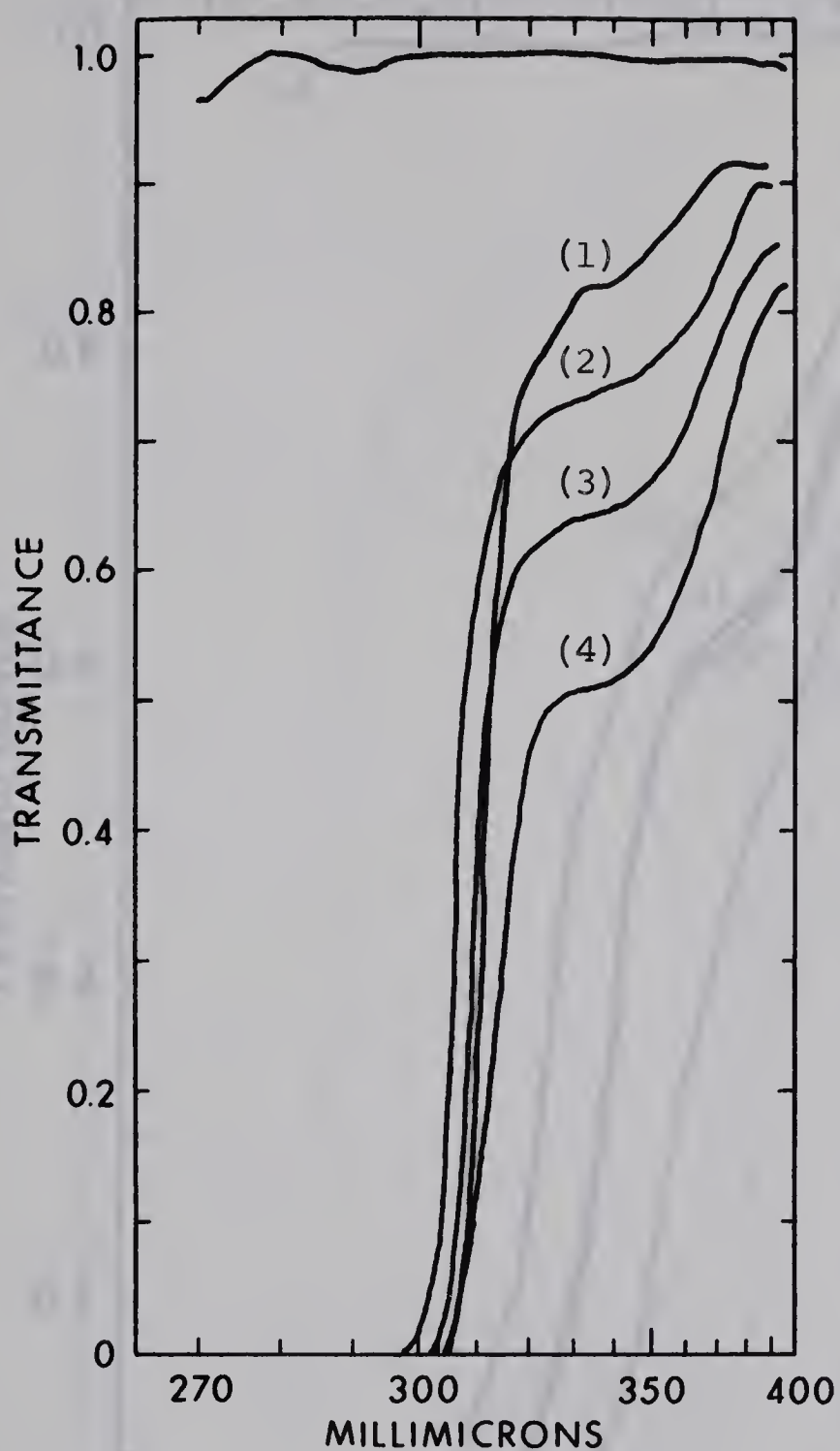


Fig.31. UV spectra of 0.5% VDEHPA in presence of different concentrations of beta-Collidine vs 0.5% VDEHPA. Spectra of beta-Collidine is also shown referred to benzene.

(1) 0.2Mol. beta-Collidine

(2) 0.02Mol. beta-Collidine

(3) 0.04Mol. beta-Collidine

(4) 0.08Mol. beta-Collidine

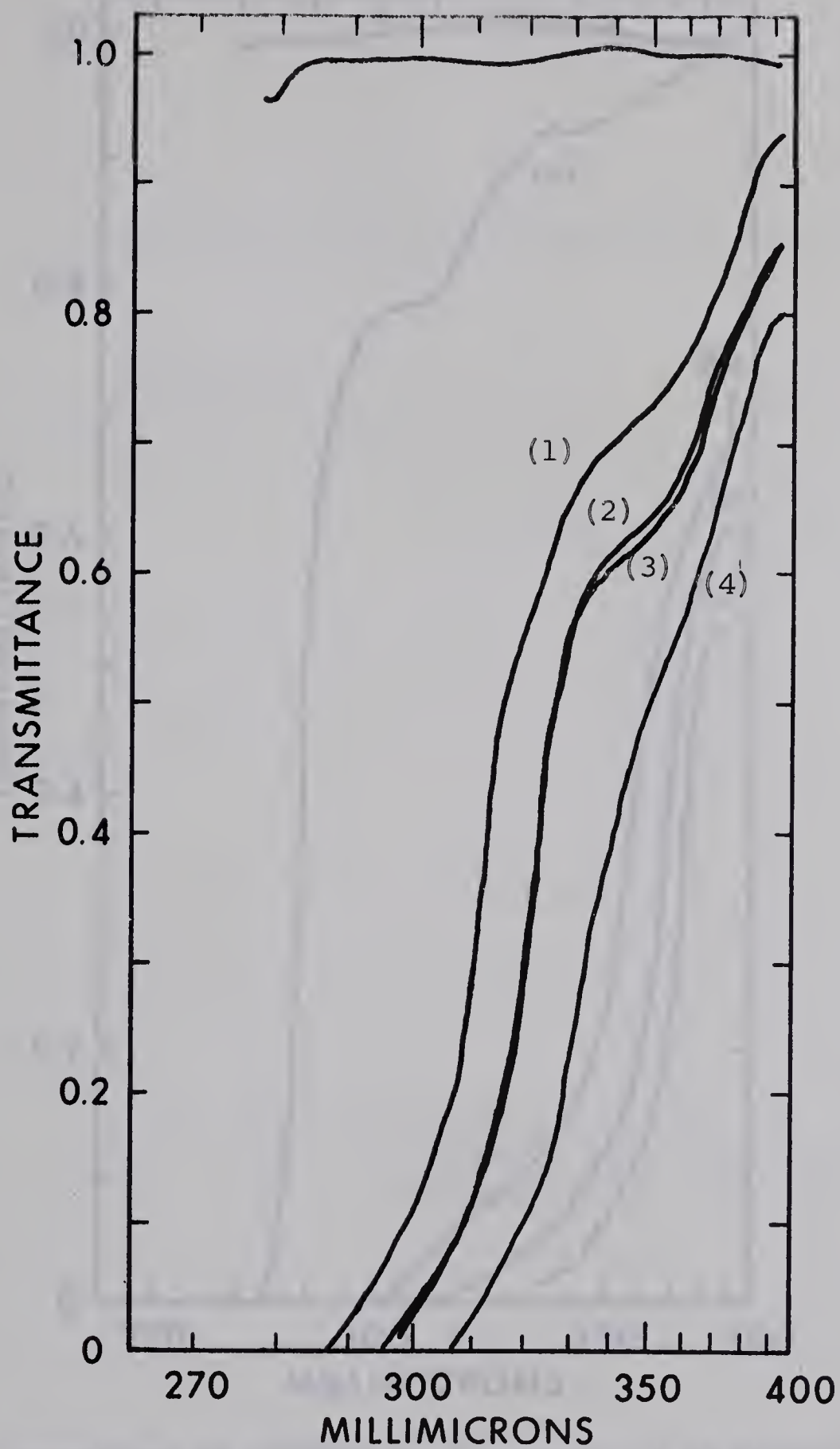


Fig.32. The UV spectrum of 0.5% VDEHPA in benzene in presence of different concentrations of 4-benzyl pyridine vs 0.5% VDEHPA in benzene.
(1) 0.02M 4BP (2) 0.04M 4BP (3) 0.05M 4BP
(4) 0.08M 4BP.

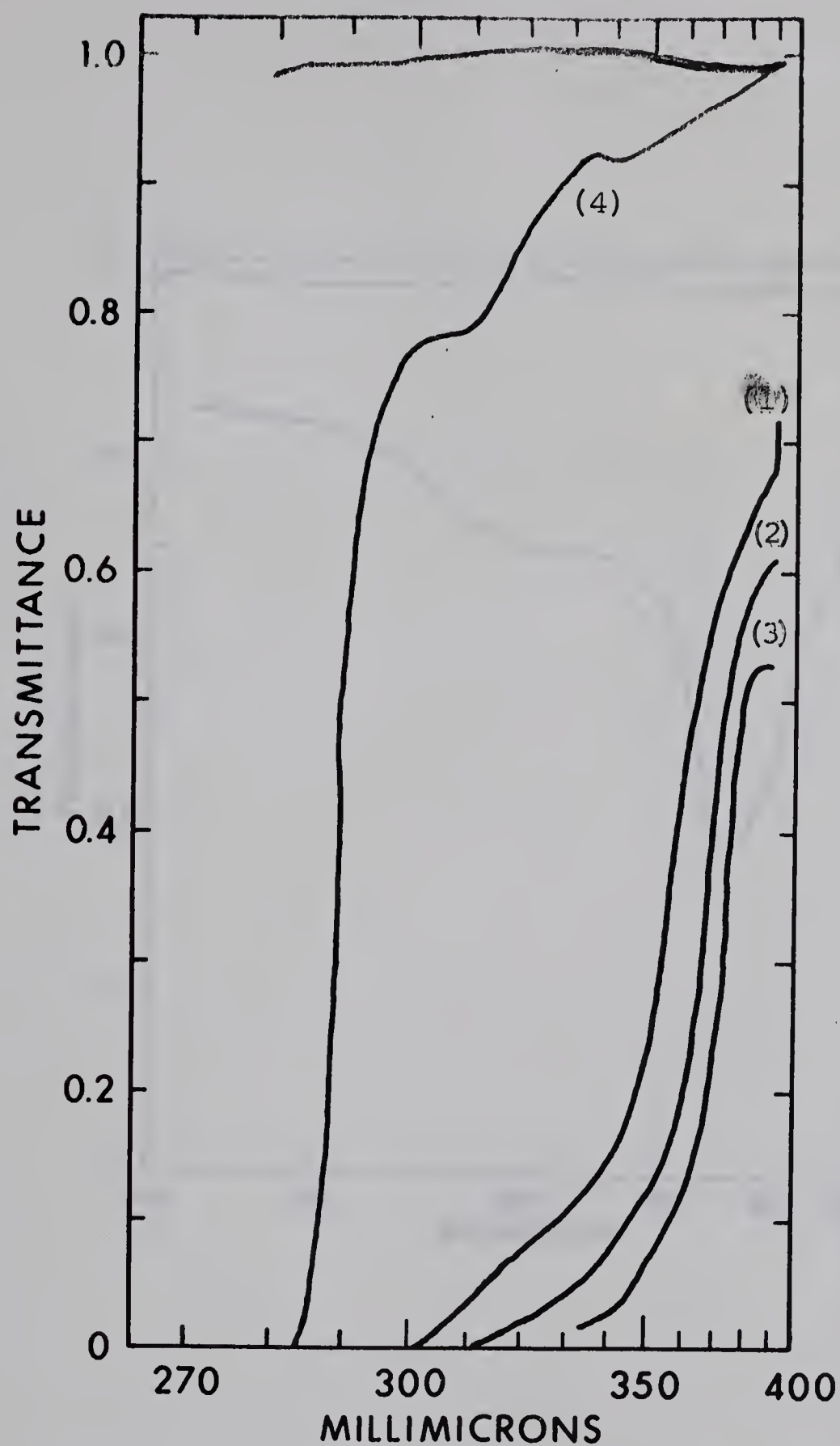


Fig.33. UV spectrum of VDEHPA in presence of different concentrations of 4 isopropyl pyridine in benzene vs benzene.

- (1) 0.125% VDEHPA + 0.05 Mol. 4IPP
- (2) 0.25% VDEHPA + 0.1 Mol. 4IPP
- (3) 0.5% VDEHPA + 0.2 Mol. 4IPP
- (4) 0.2 Mol. 4IPP in benzene

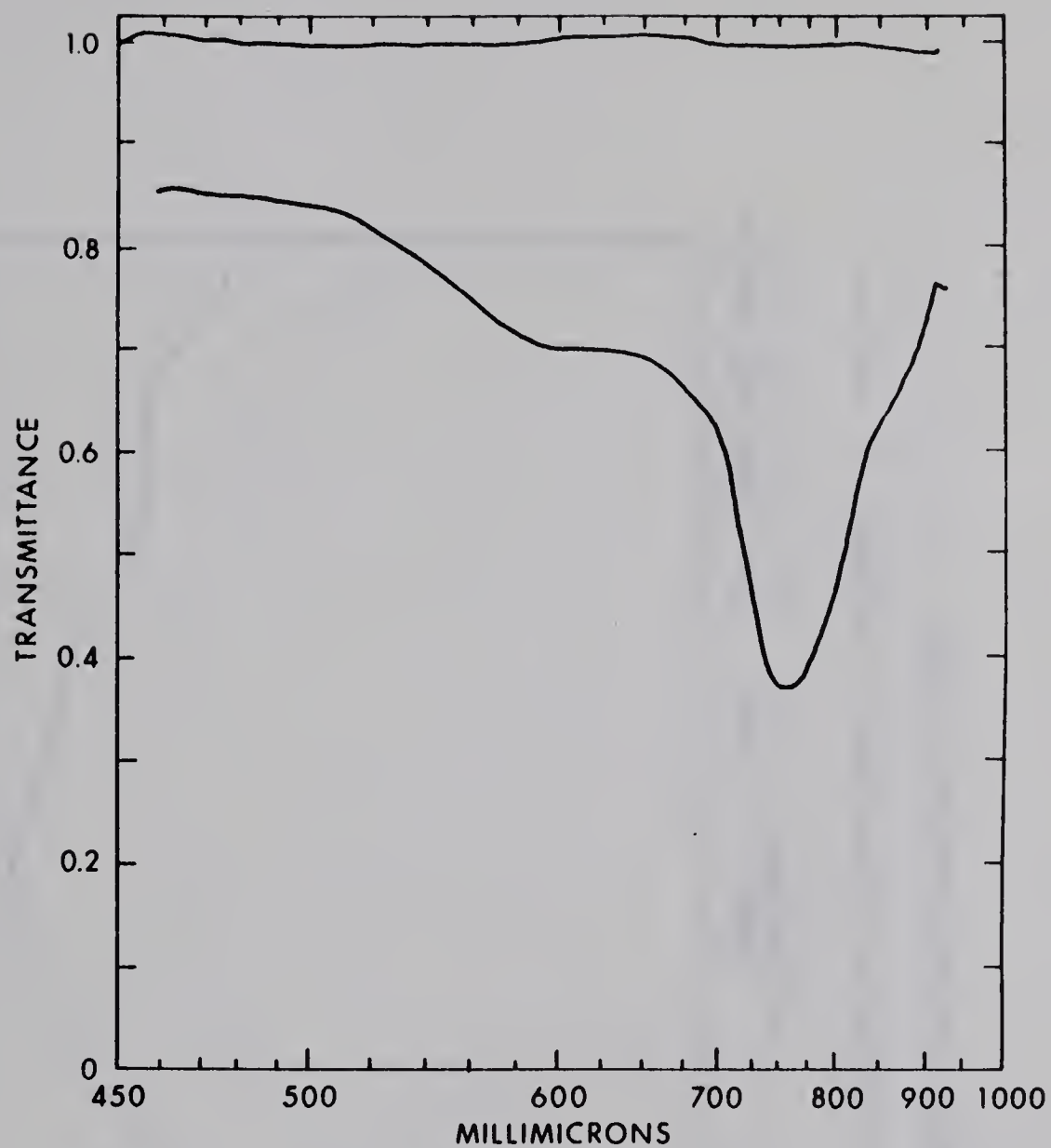


Fig.34(a) . Visible absorption spectrum of 1.25%
VDEHPA in 4EP vs 4EP.

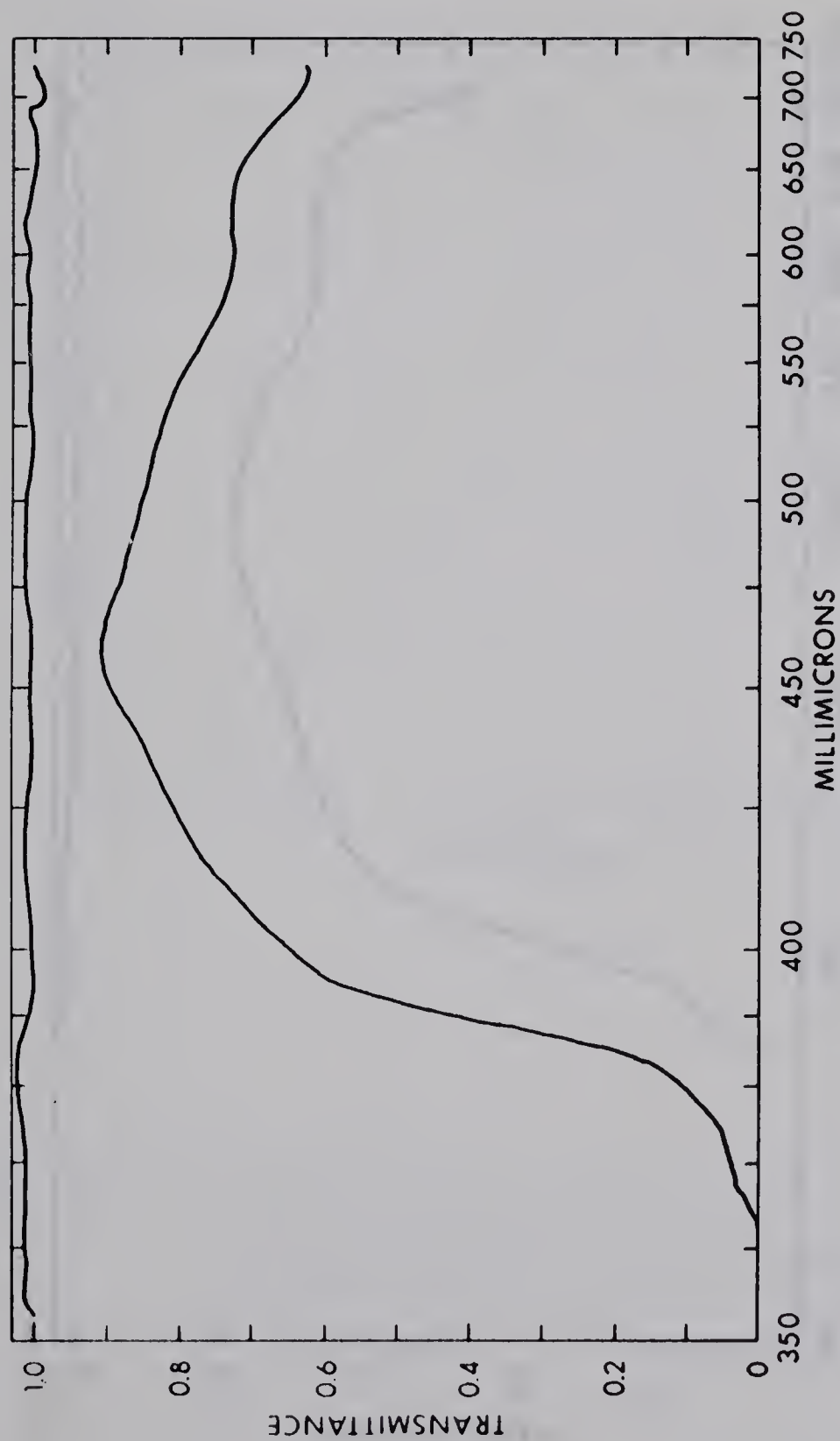


Fig.34 (b) Visible absorption spectrum of VDEHPA in 4EP vs 4EP, VDEHPA concentration 1.25%.

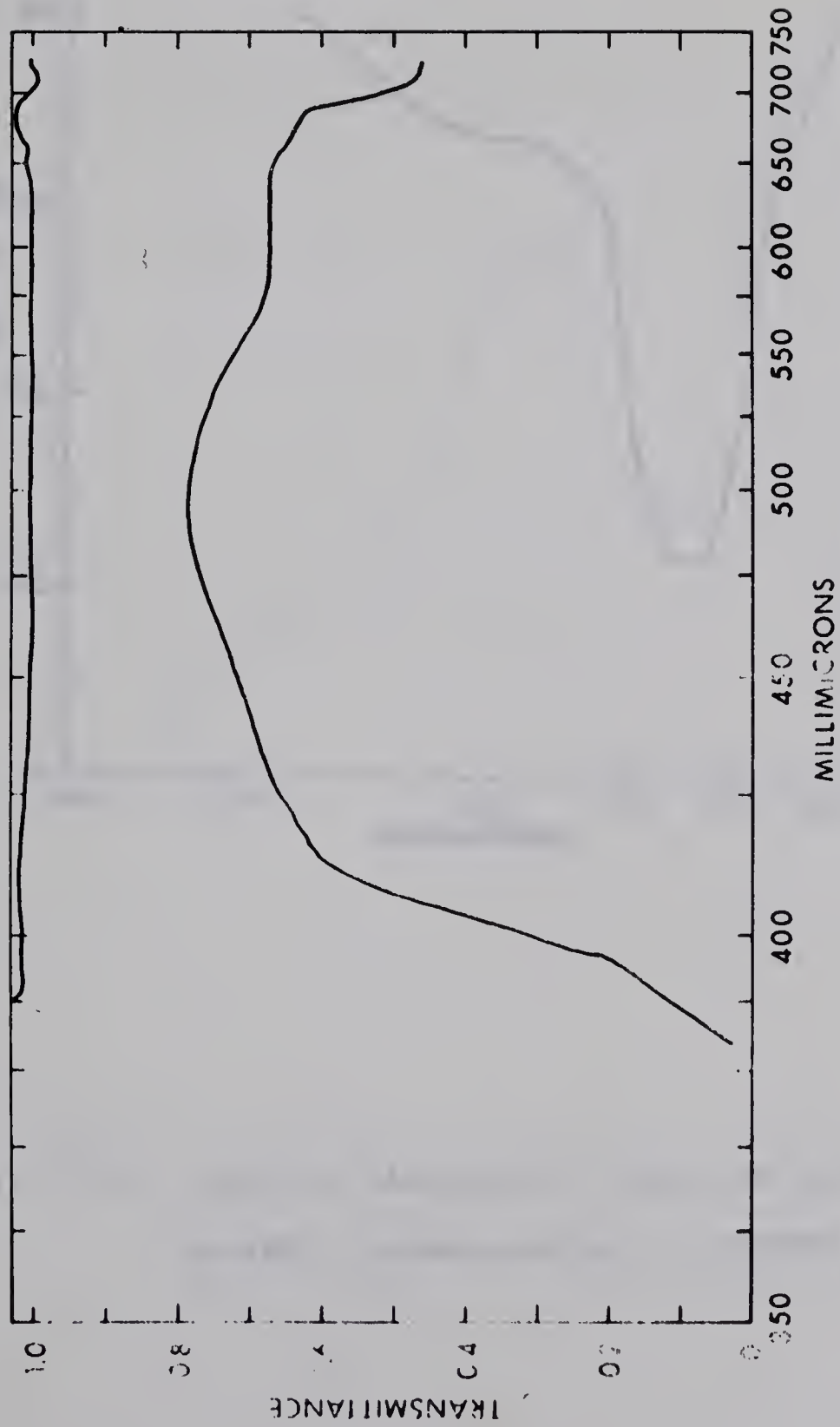


Fig.35(a). Visible absorption spectrum of 1.25% VDEHPA in

4BP vs 4BP.

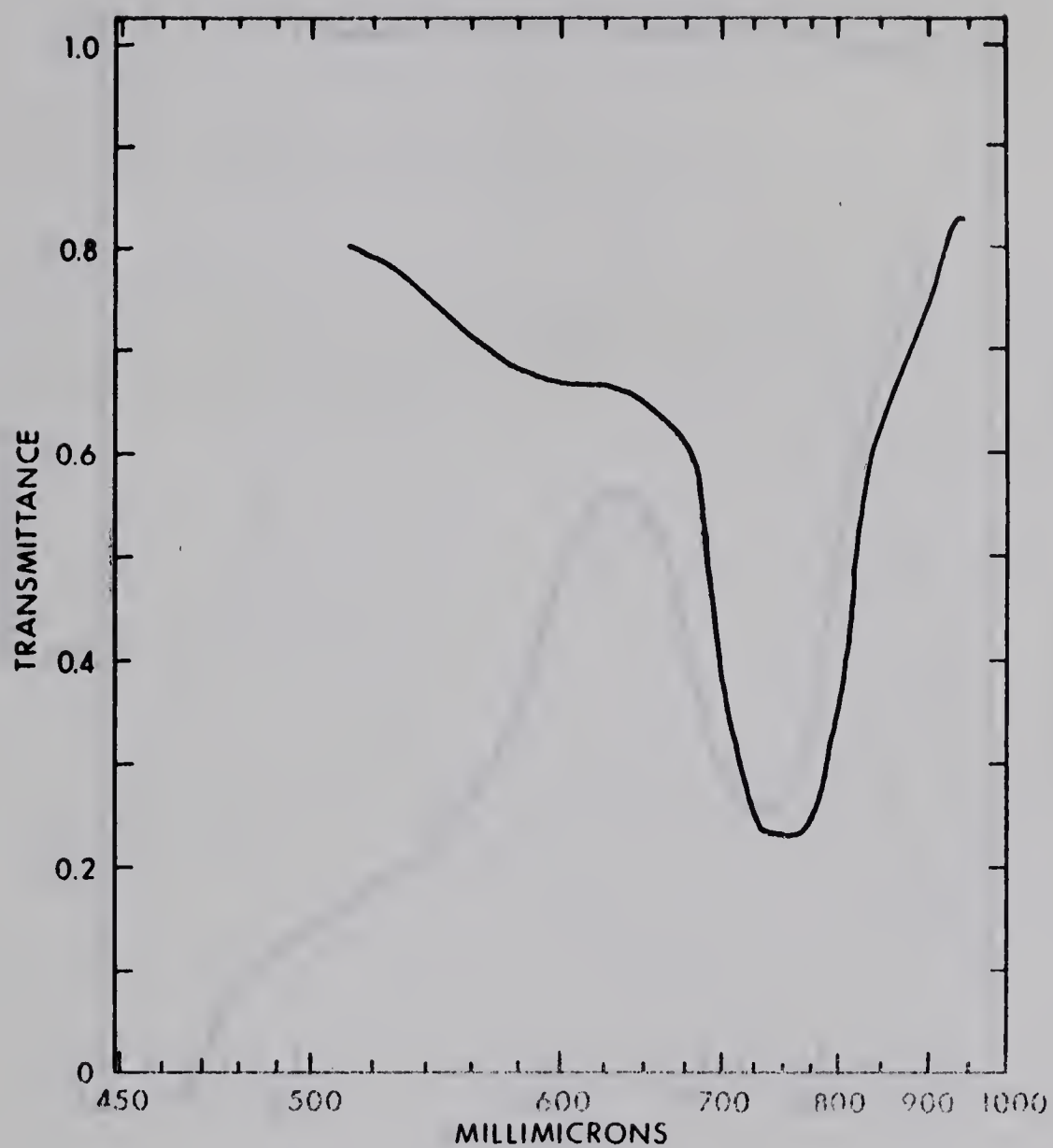


Fig.35(b) . Visible absorption spectrum of VDEHPA in 4BP
vs 4BP. Concentration of VDEHPA 1.25%.

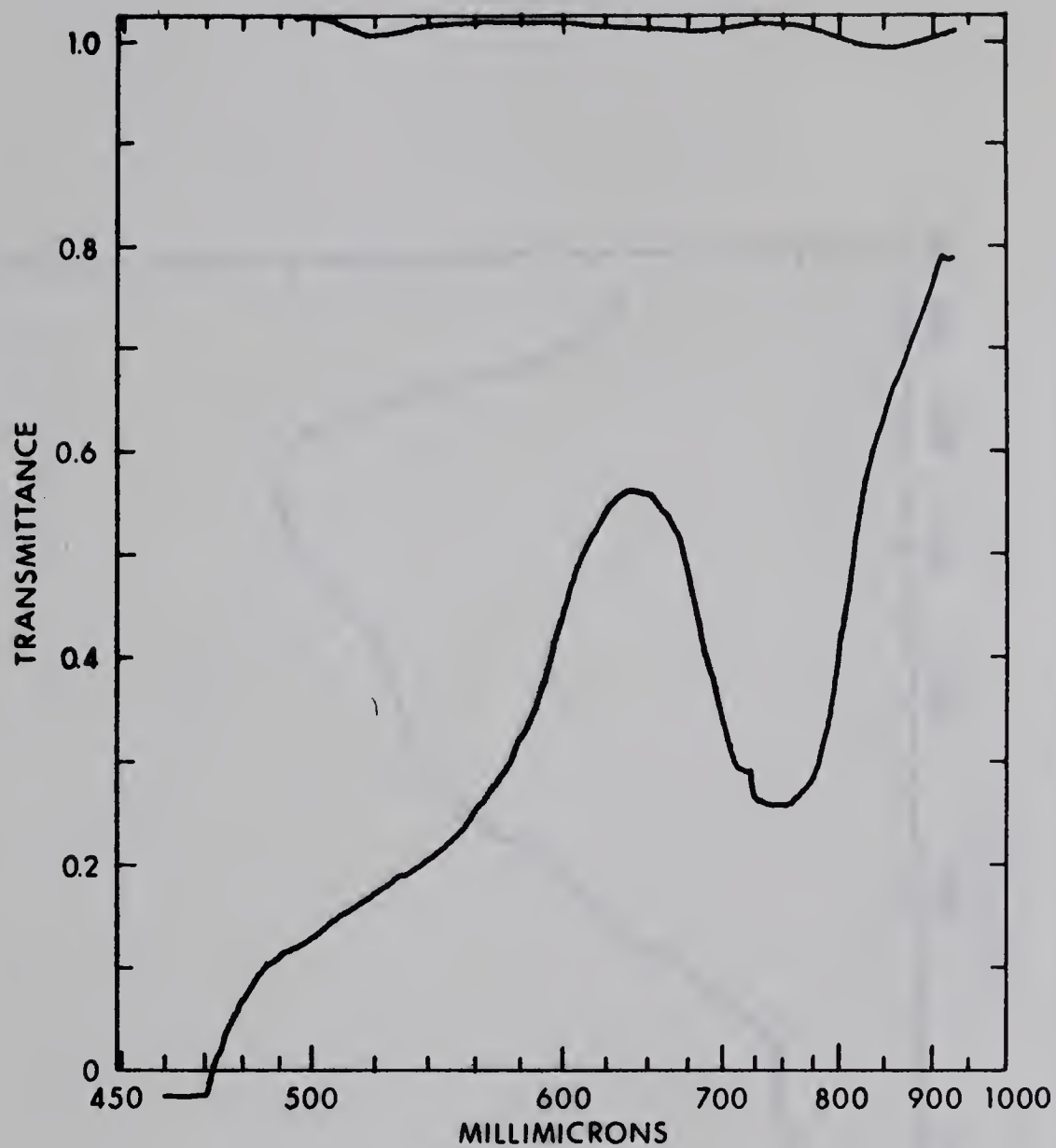


Fig. 36(a) Visible absorption spectrum of VDEHPA in
beta-Collidine vs beta-Collidine.
Concentration of 1.25% VDEHPA.

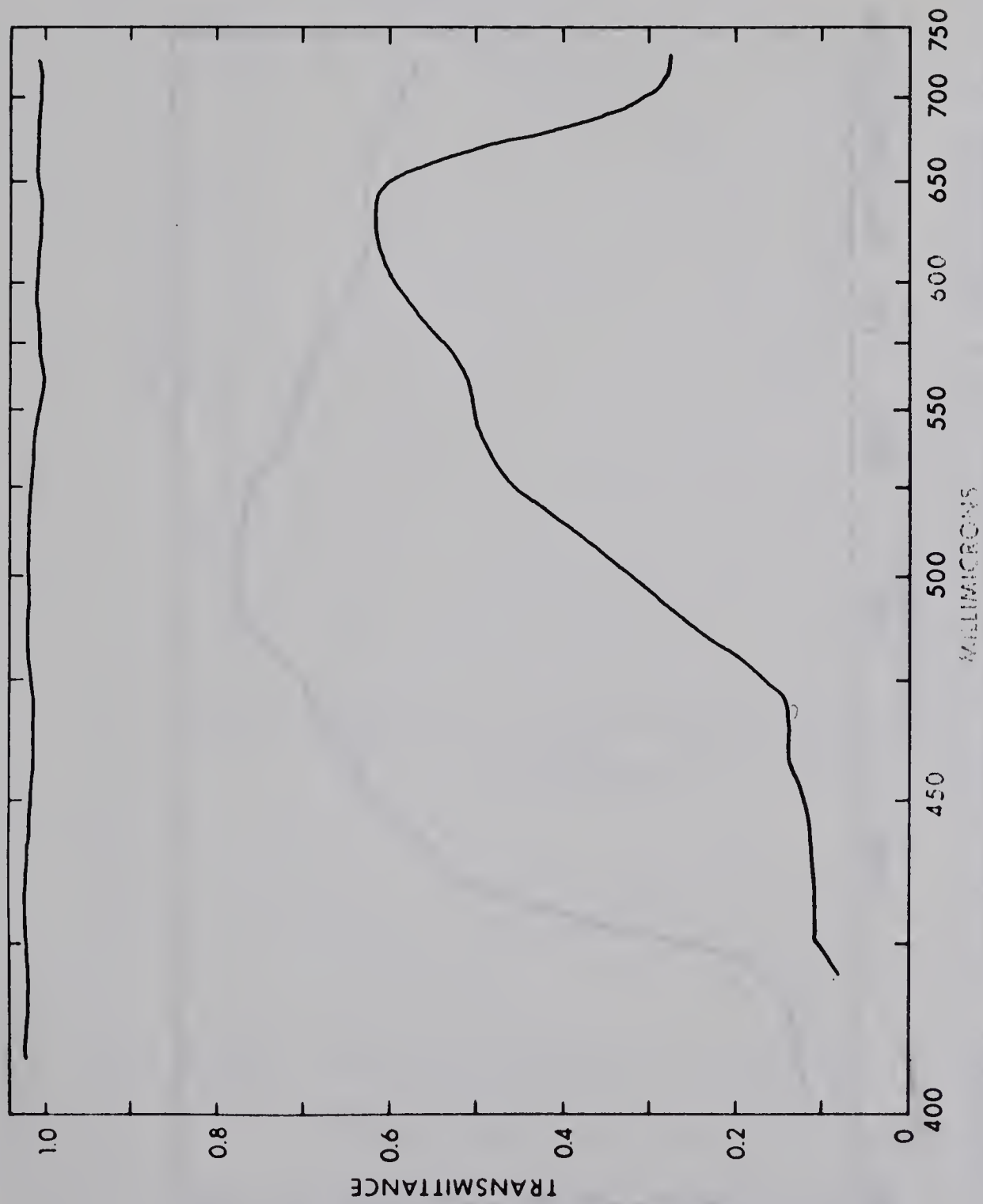


Fig.36(b) . Visible absorption spectrum 1.25% VDEHPA in
beta-Collidine vs beta-Collidine.

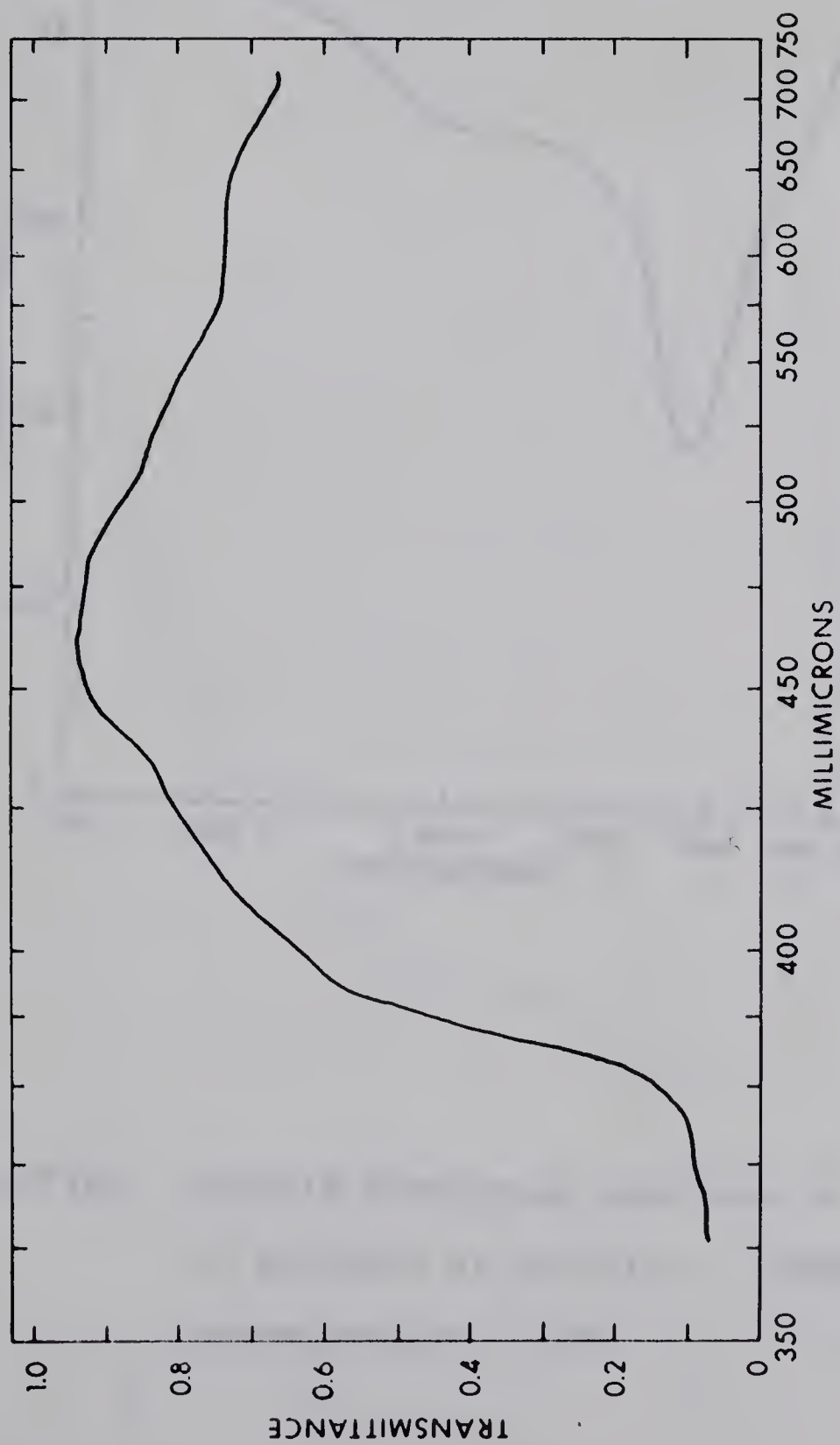


Fig.37(a). Visible absorption spectrum of 1.25% VDEHPA in pyridine vs pyridine.

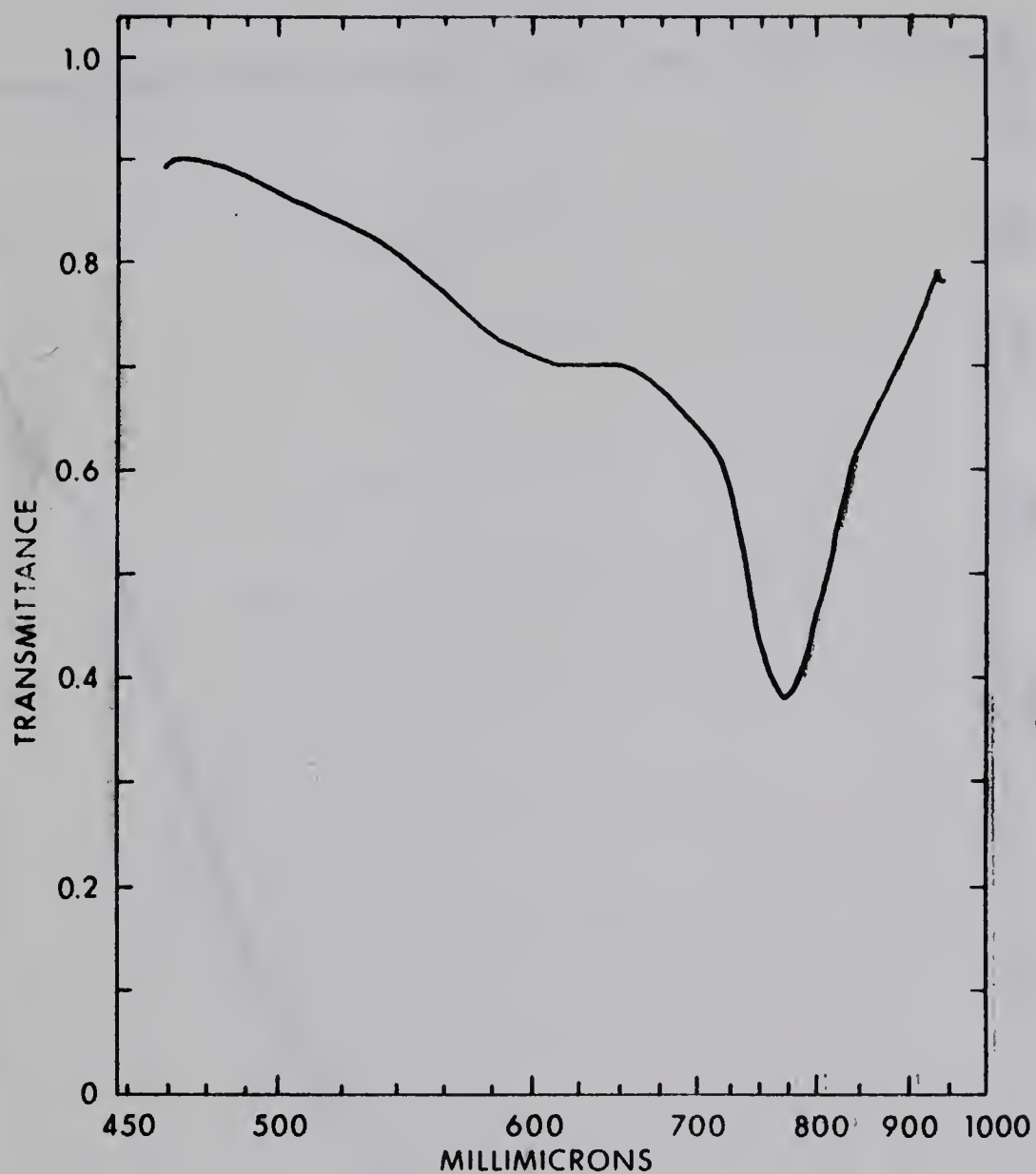


Fig.37(b) . Visible absorption spectrum of VDEHPA
in pyridine vs pyridine. VDEHPA
concentration 1.25%.

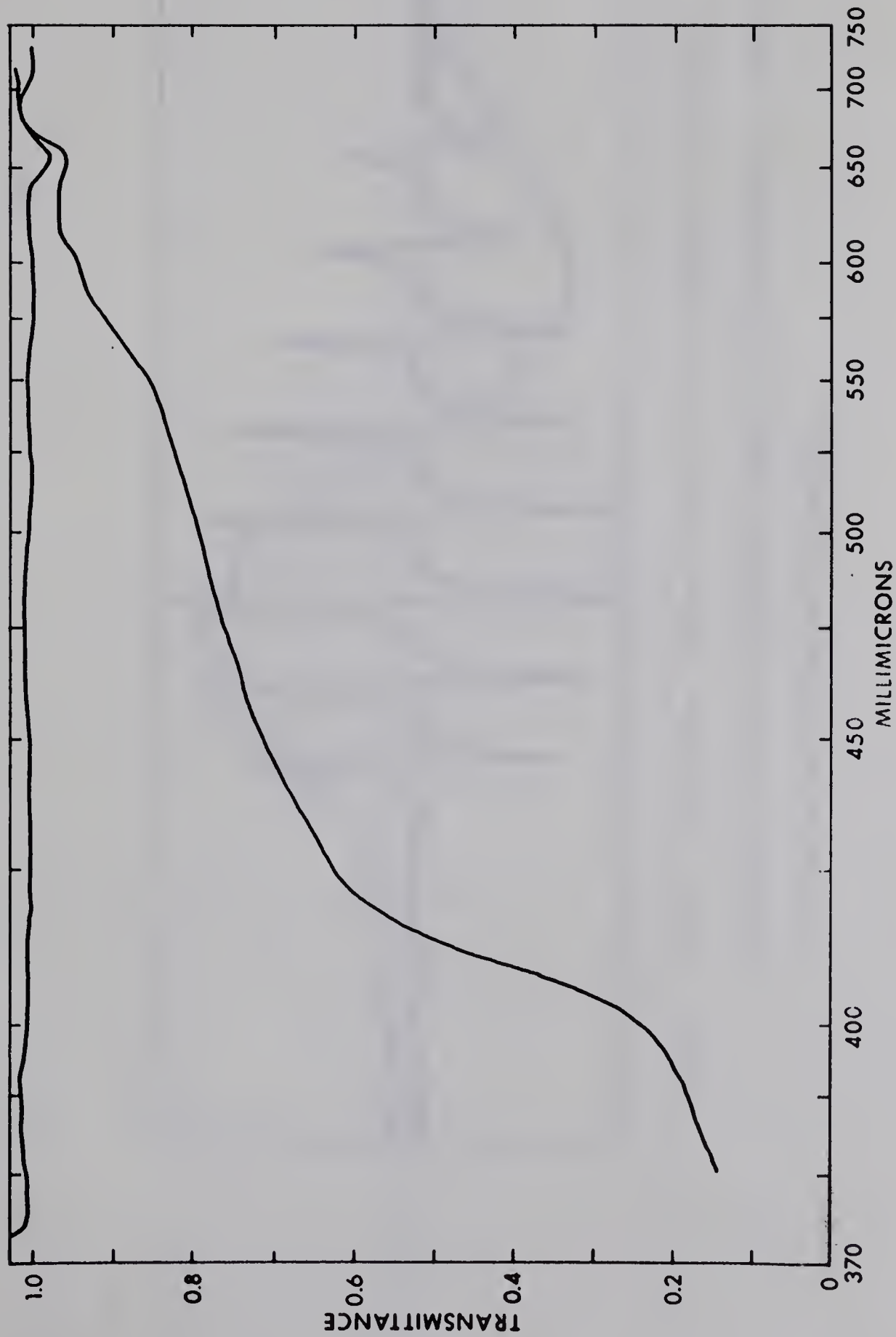


Fig.38. Visible absorption spectrum of 1.25% VDEHPA in 4IPP
(4 isopropyl pyridine) .

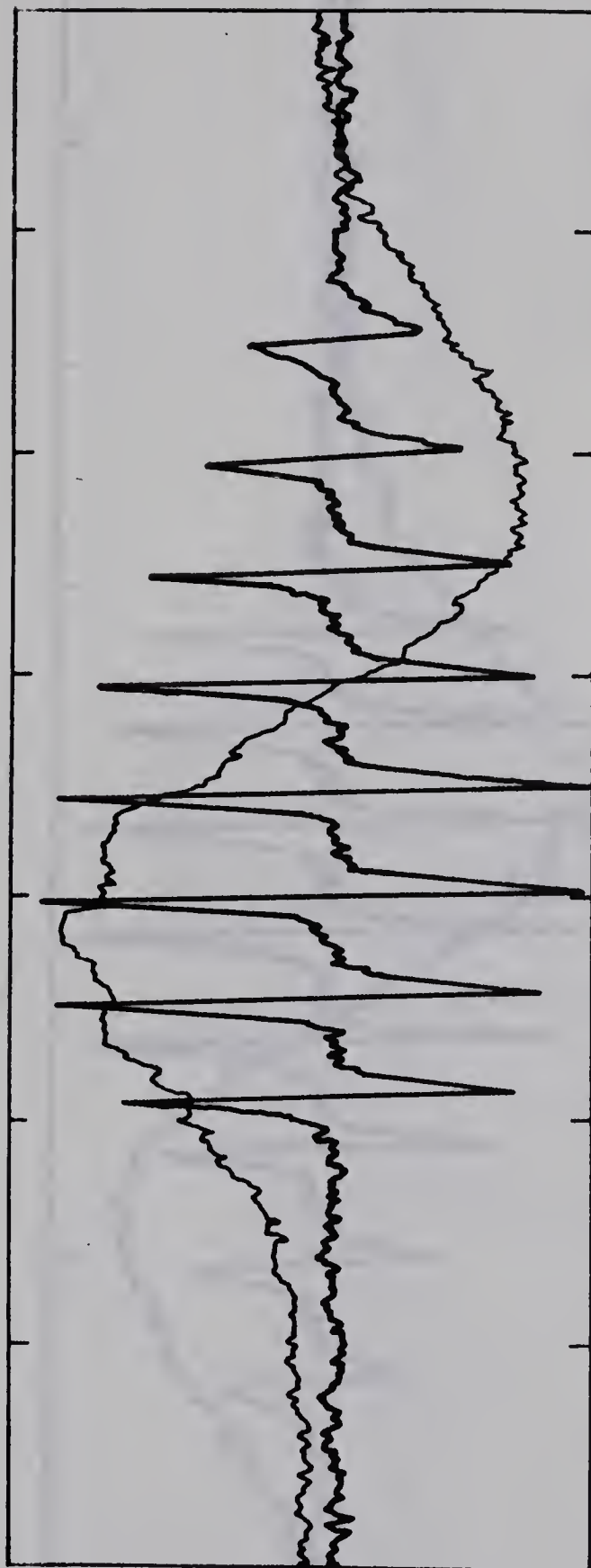


Fig.39. E.P.R. spectrum (fine line) of 2.5% VDEHPA in benzene. The distance between adjacent bars is 250 gauss. Heavy line indicates spectrum of $\text{VO}(\text{aca})_2$.

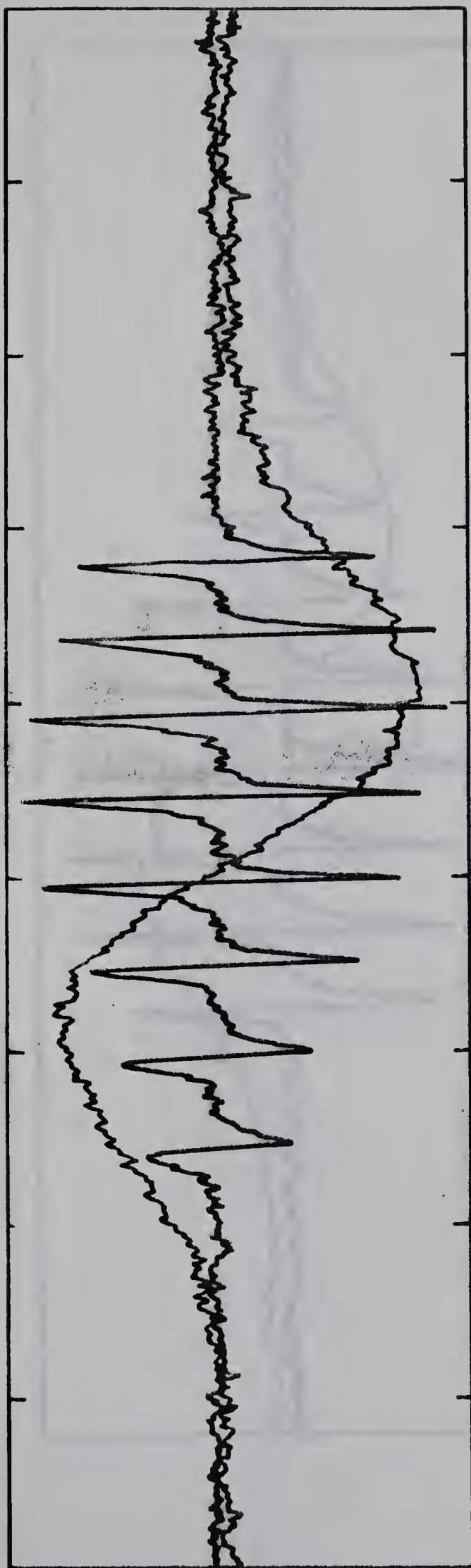


Fig.40. E.P.R. spectrum (fine line) of 2.5% VDEHPA in 2EP compared with the spectrum (heavy line) of VO(aca)₂ in benzene. Distance between adjacent bars 250 gauss.

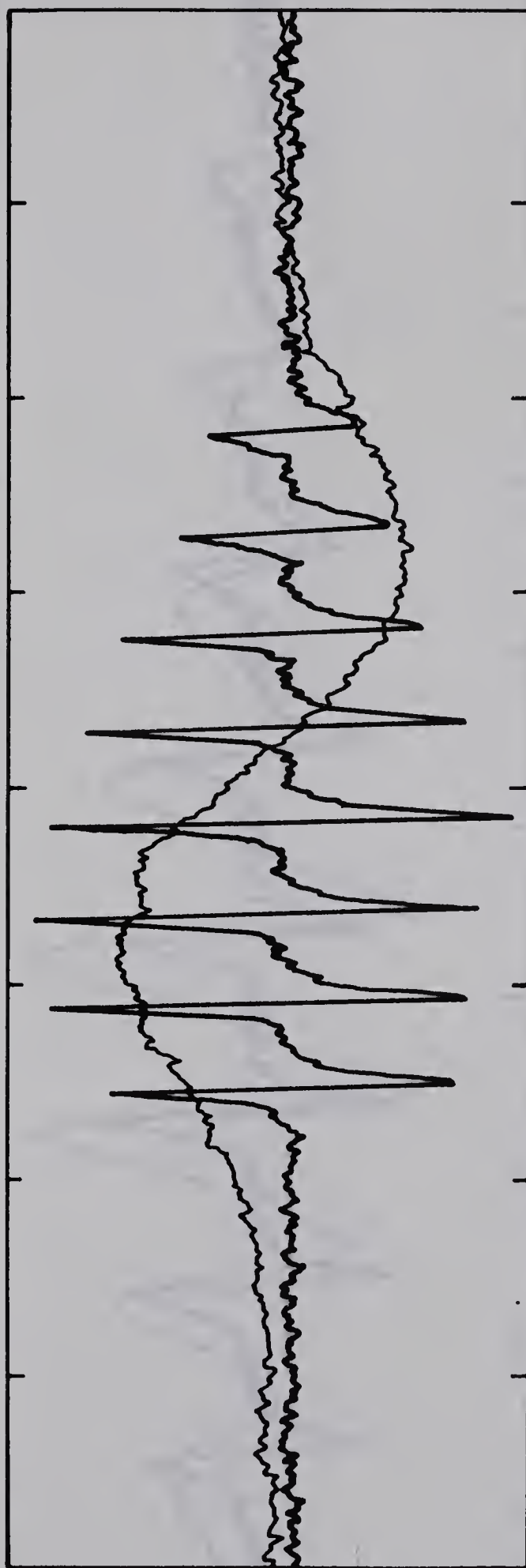


Fig.41. E.P.R. spectrum (fine line) of 2.5% VDEHPA in 2BP compared with the spectrum (heavy line) of VO(aca)₂ in benzene. Distance between adjacent bars 250 gauss.

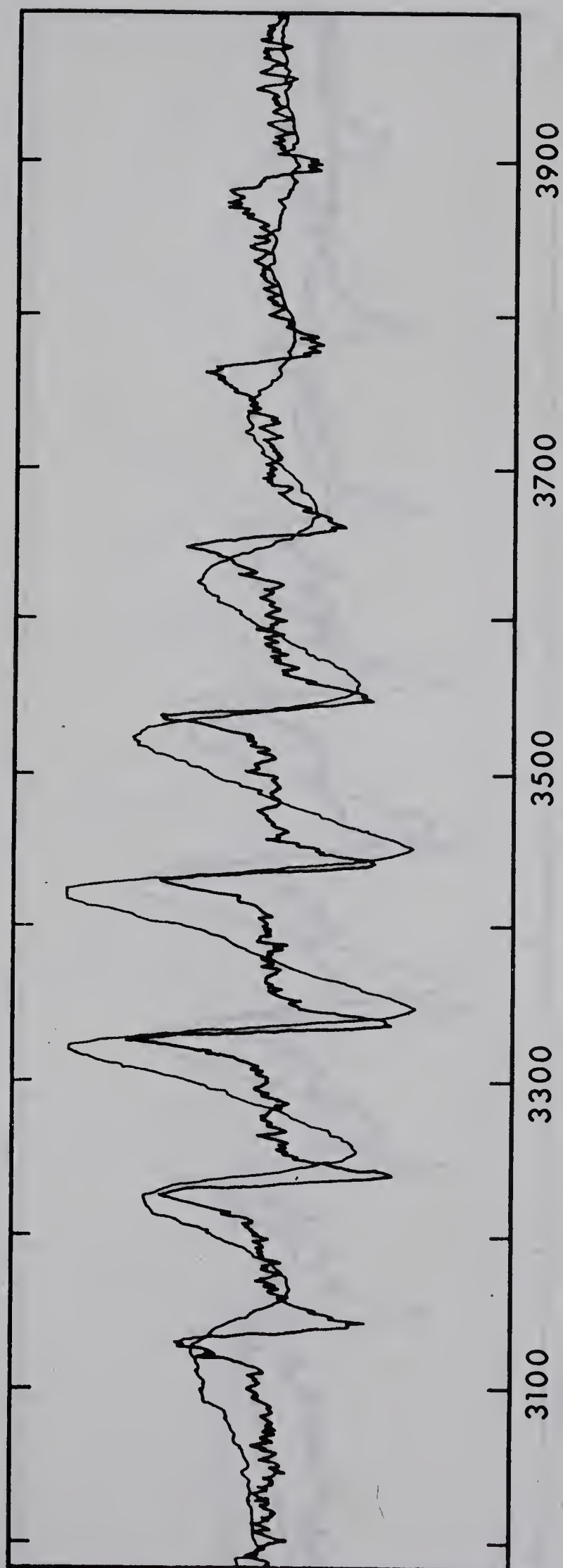


Fig.42. E.P.R. spectrum (fine line) of 2.5% VDEHPA in pyridine compared with the spectrum (heavy line) of $\text{VO}(\text{aca})_2$ in benzene.

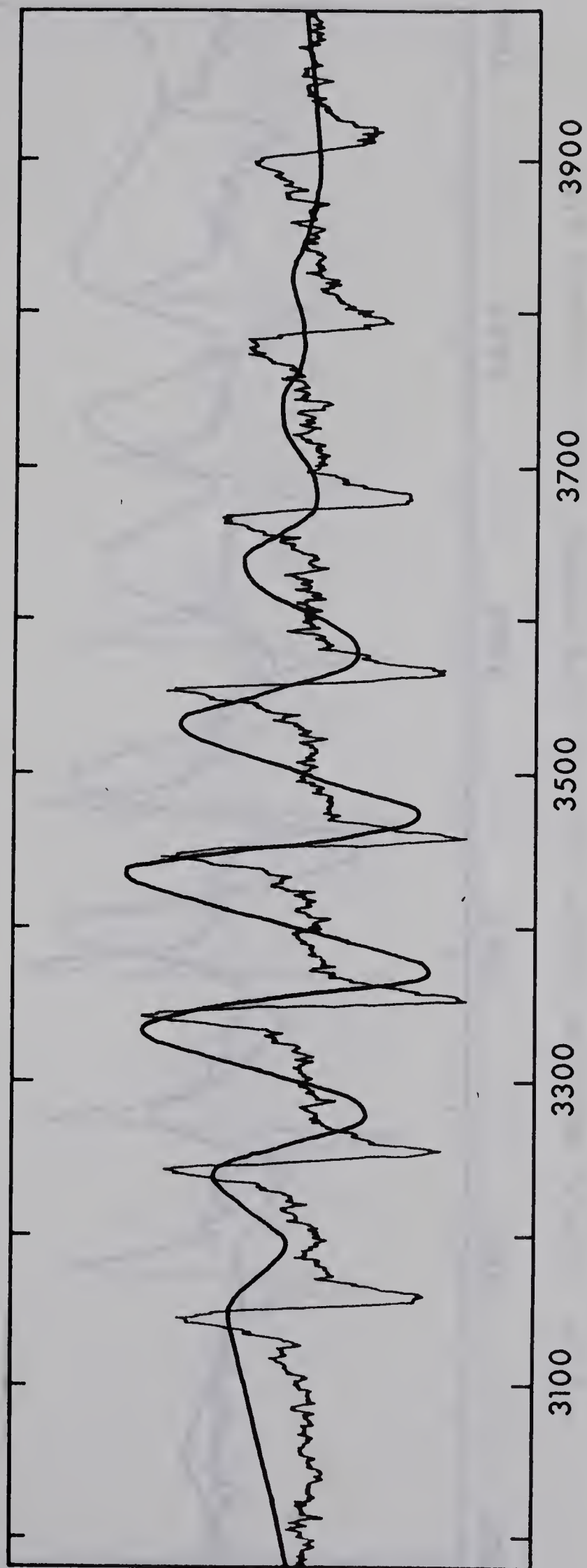


Fig 43 E.P.R. spectrum (heavy line) of 2.5% VDEHPA in 4EP compared with the spectrum (fine line) of VO(aca)₂ in benzene

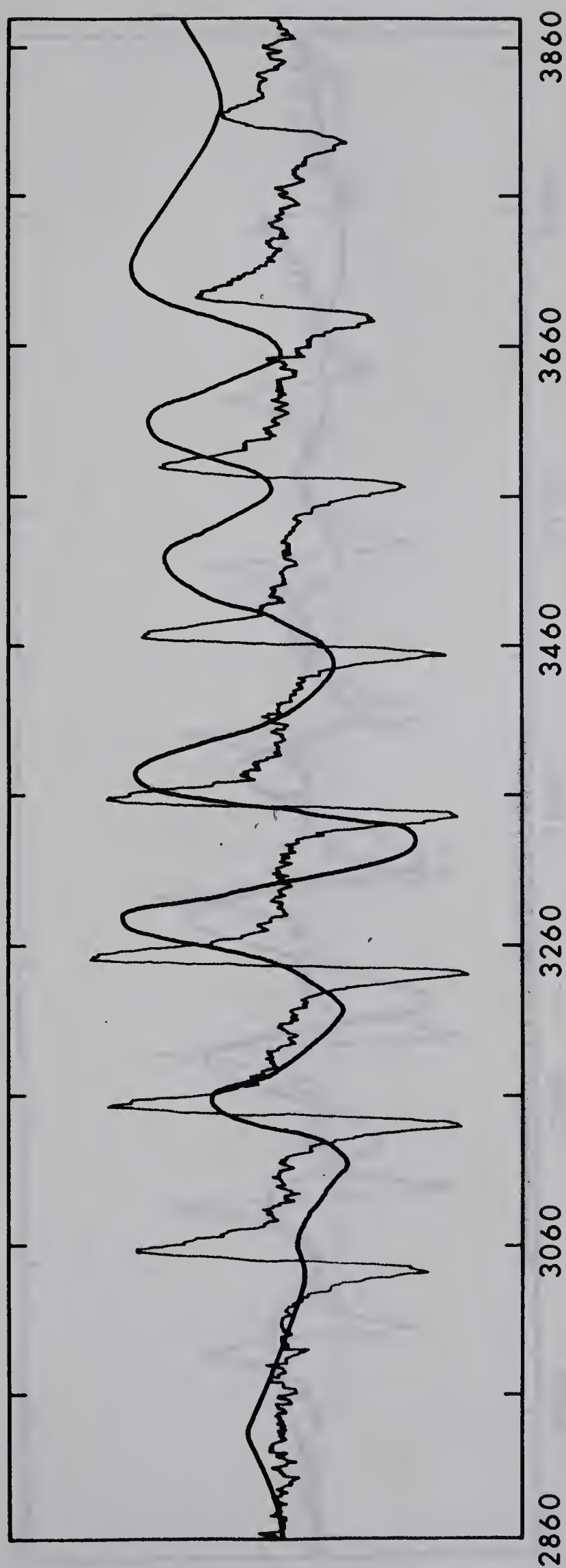


Fig.44. E.P.R. spectrum (heavy line) of 2.5% VDEHPA in 4BP compared with the spectrum (fine line) of VO(aca)₂ in benzene.

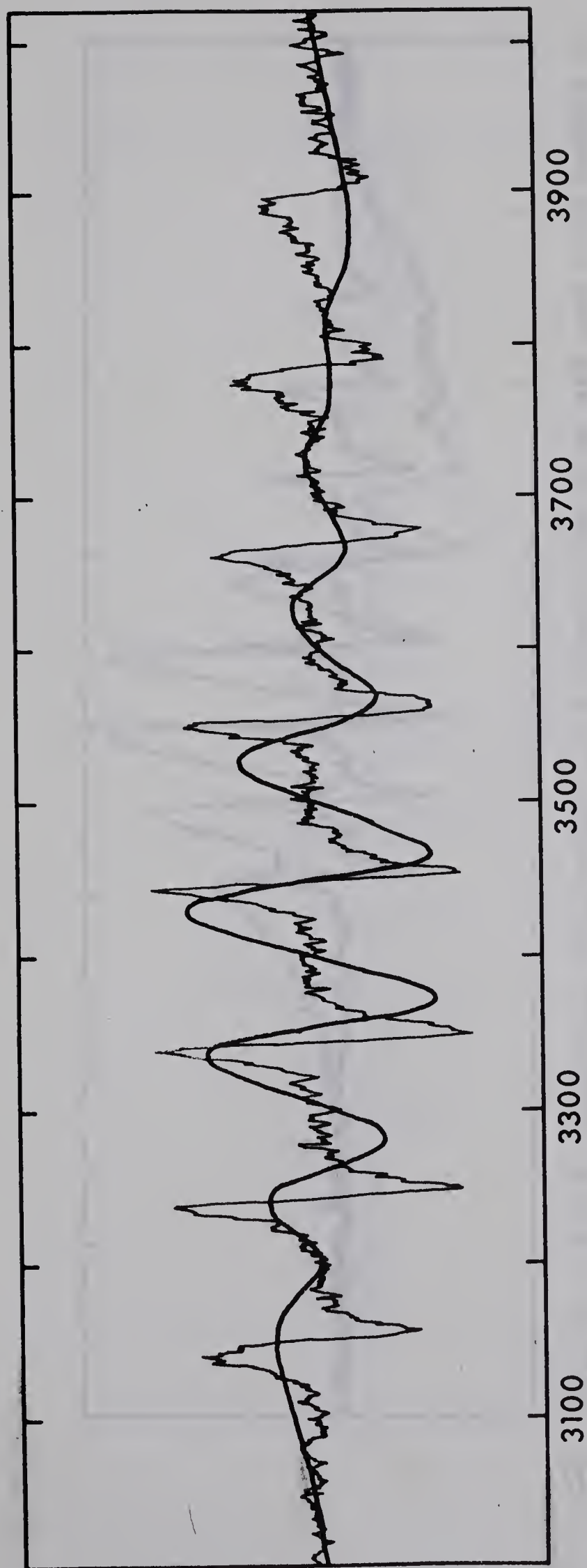


Fig 45 E.P.R. spectrum (heavy line) of 2 5% VDEHPA in beta-Collidine compared with the spectrum (fine line) of VO(aca)₂ in benzene

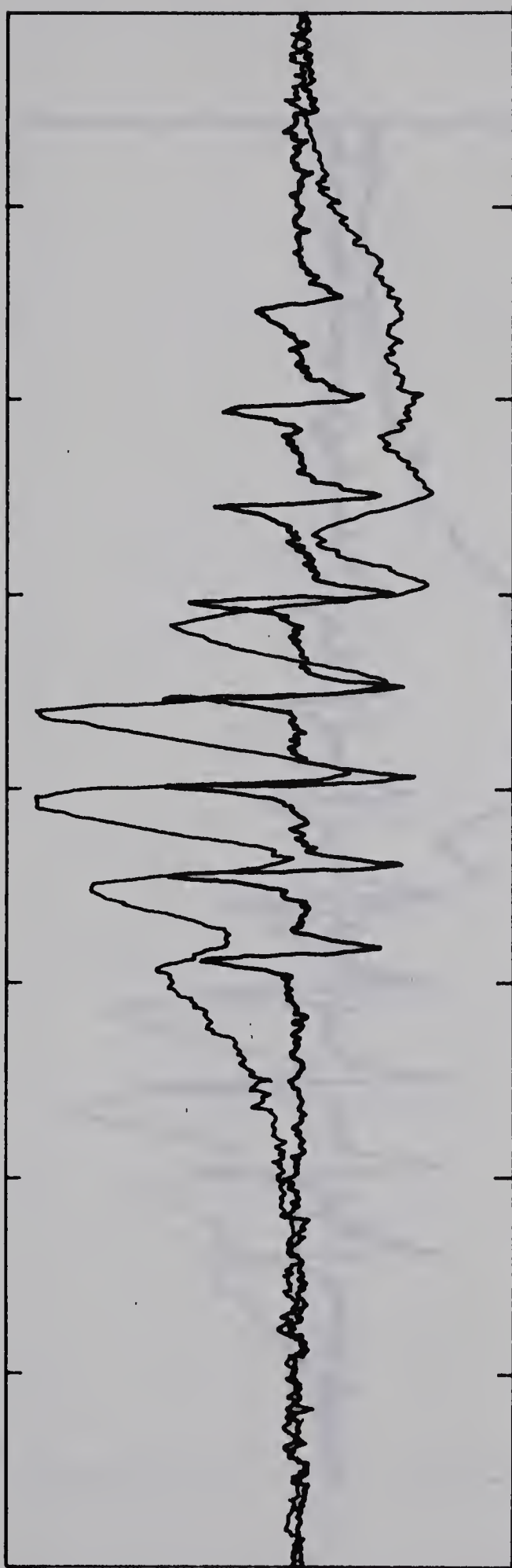


Fig.46. E.P.R. spectrum (fine line) of a mixture of 0.2M 4EP and 2.5% VDEHPA in benzene solution compared with the spectrum (heavy line) of $\text{VO}(\text{aca})_2$ in benzene. Distance between adjacent bars 250 gauss.

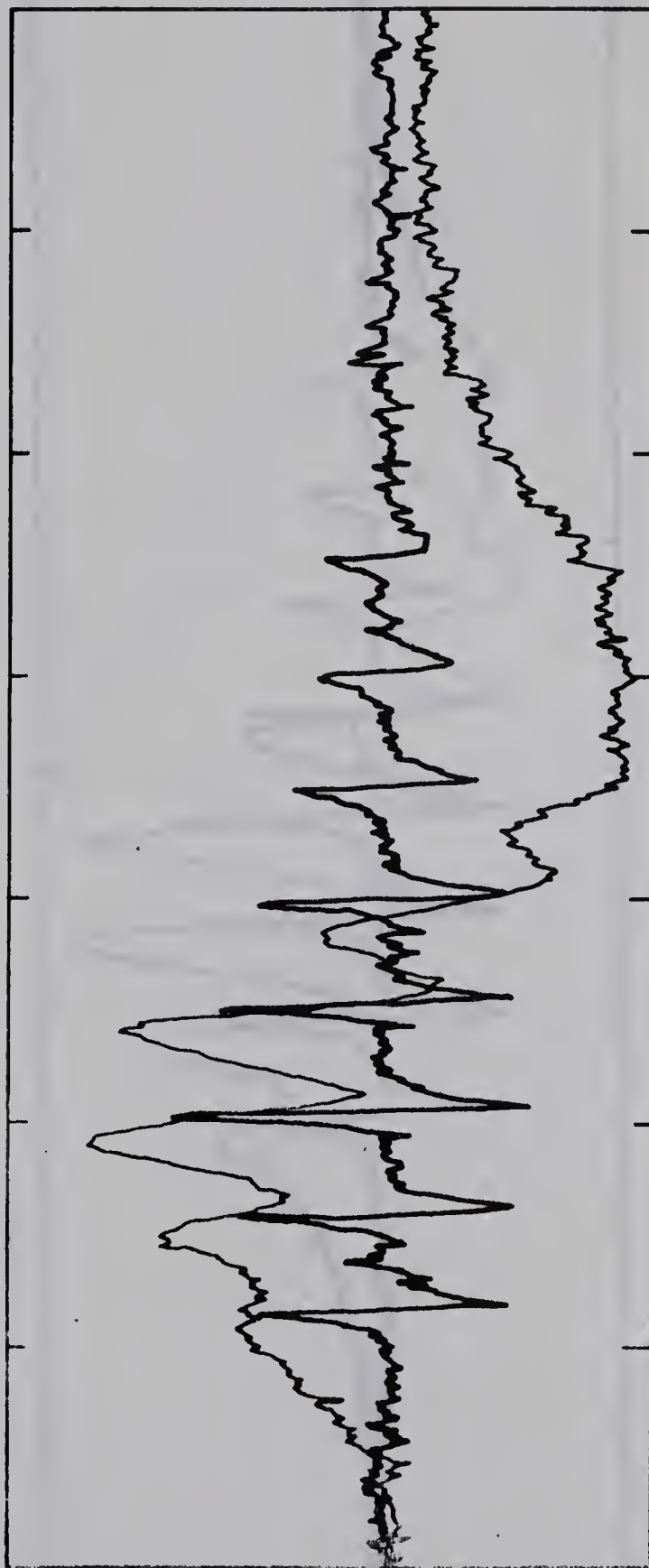


Fig.47. E.P.R. spectrum (fine line) of a mixture of 0.2M 4BP and 2.5% VDEHPA in benzene solution compared with the spectrum (heavy line) of VO(aca)₂ in benzene. Distance between adjacent bars 250 gauss.

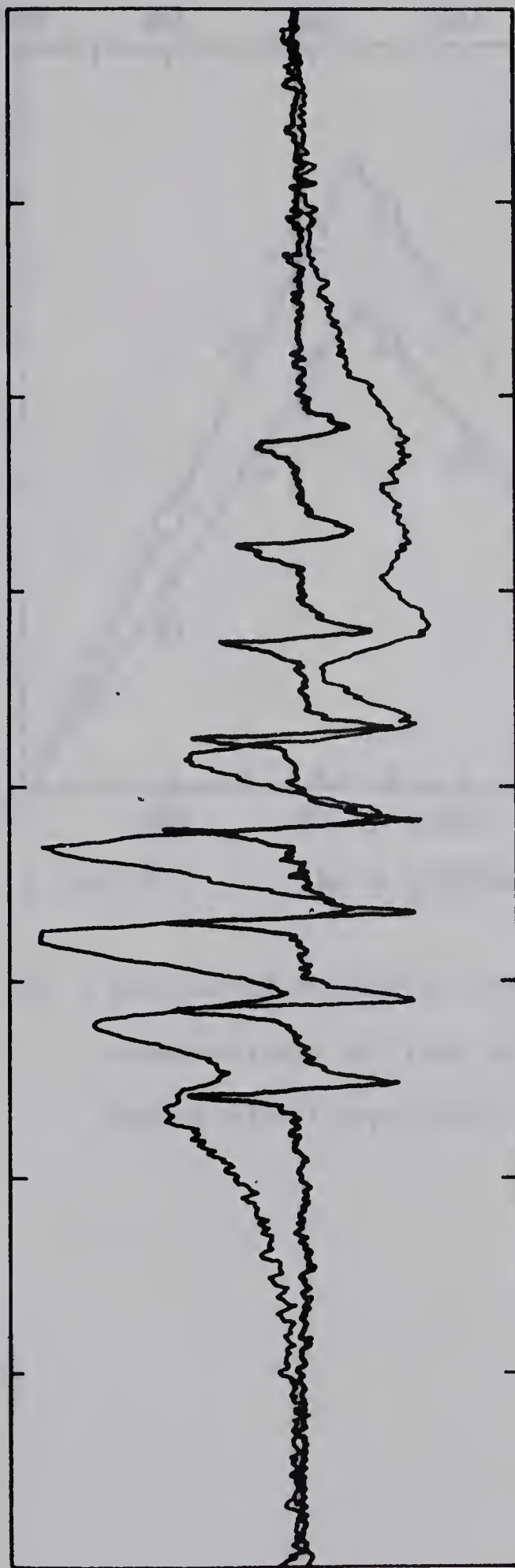


Fig.48. E.P.R. spectrum (fine line) of 0.2M beta-Collidine and 2.5% VDEHPA in benzene solutions compared with the spectrum (heavy line) of VO(aca)₂ in benzene. Distance between adjacent bars 250 gauss.

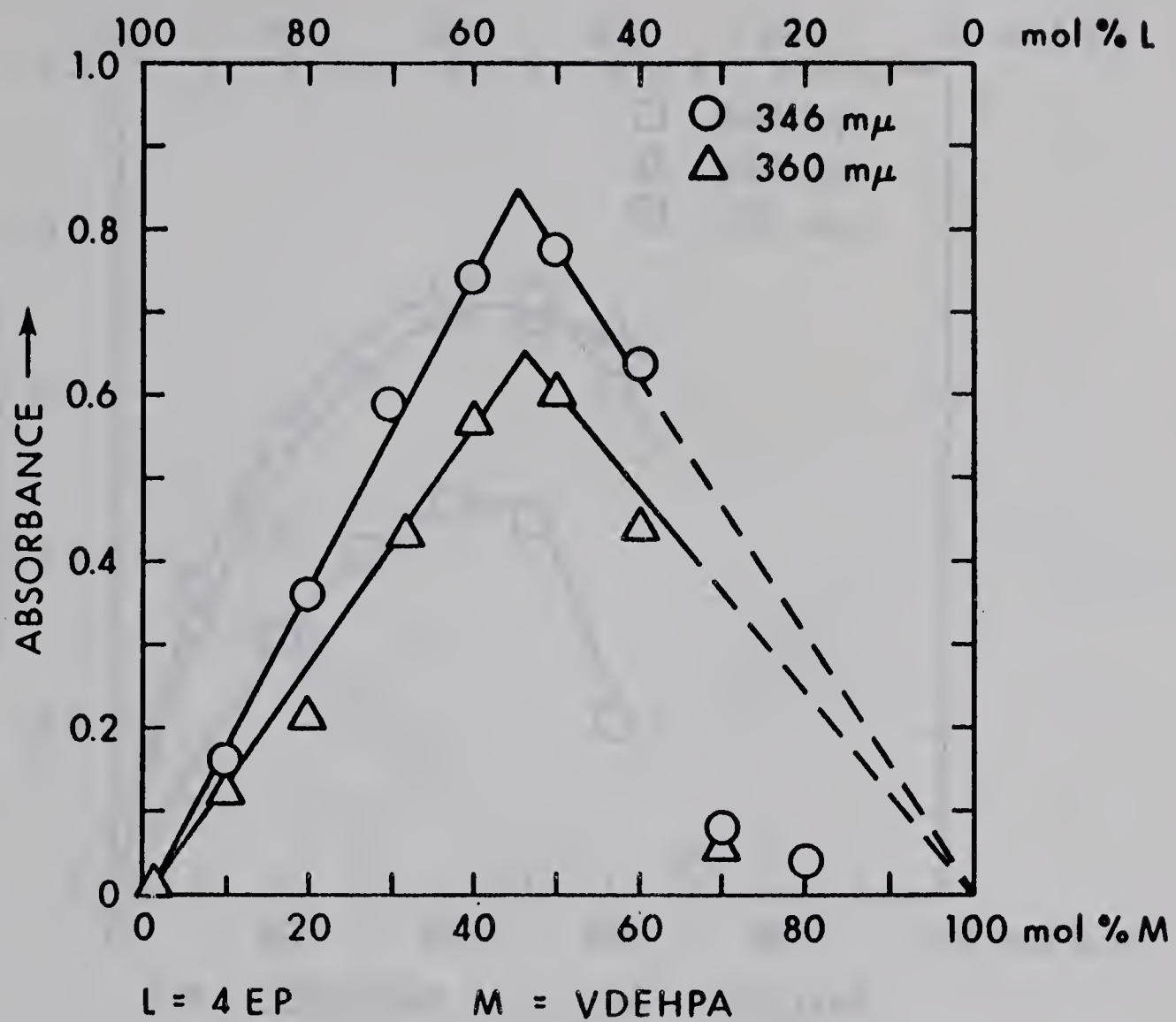


Fig. 49. Spectrophotometric determination of the composition of the adduct between VDEHPA and 4-ethyl pyridine.

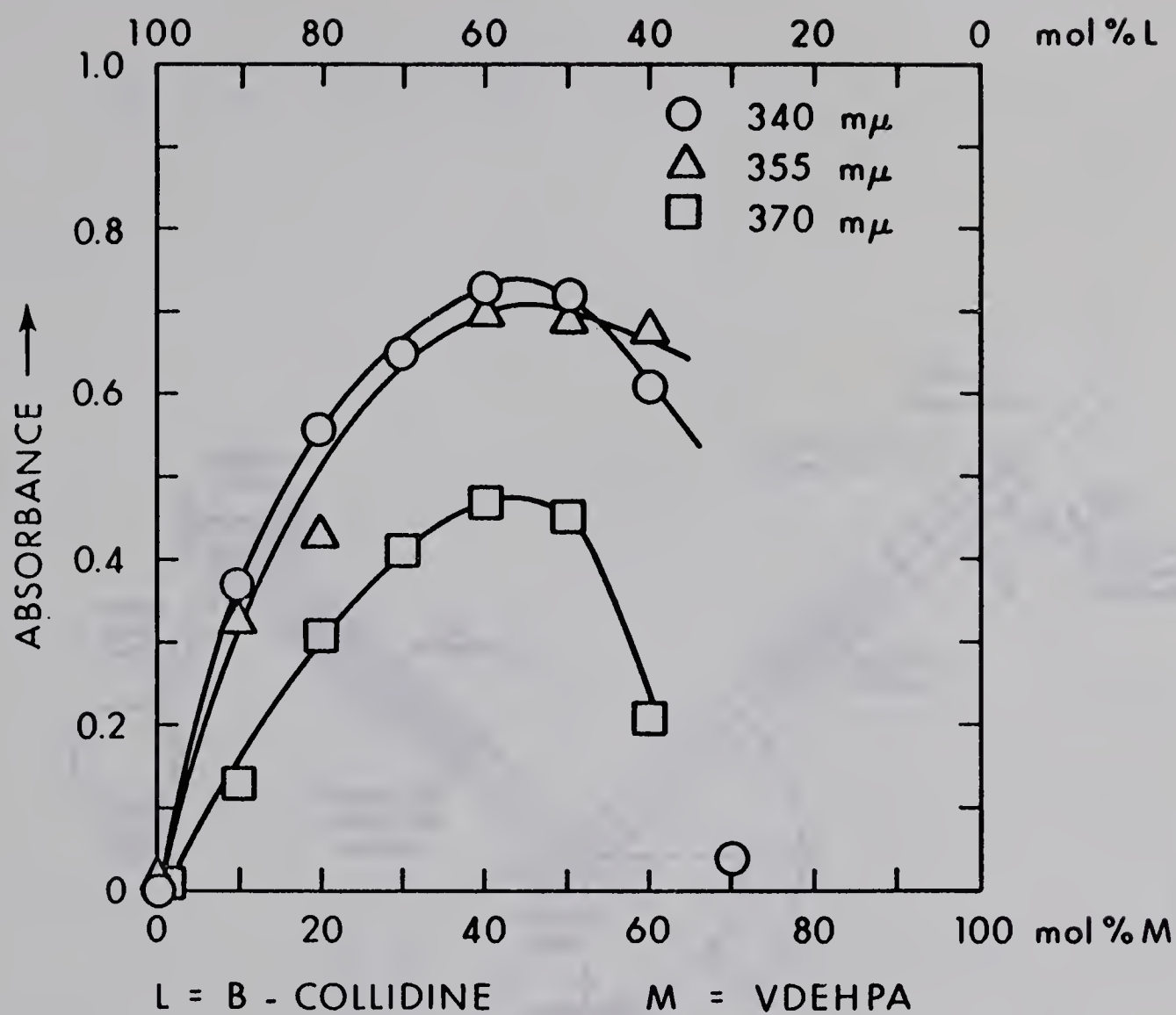
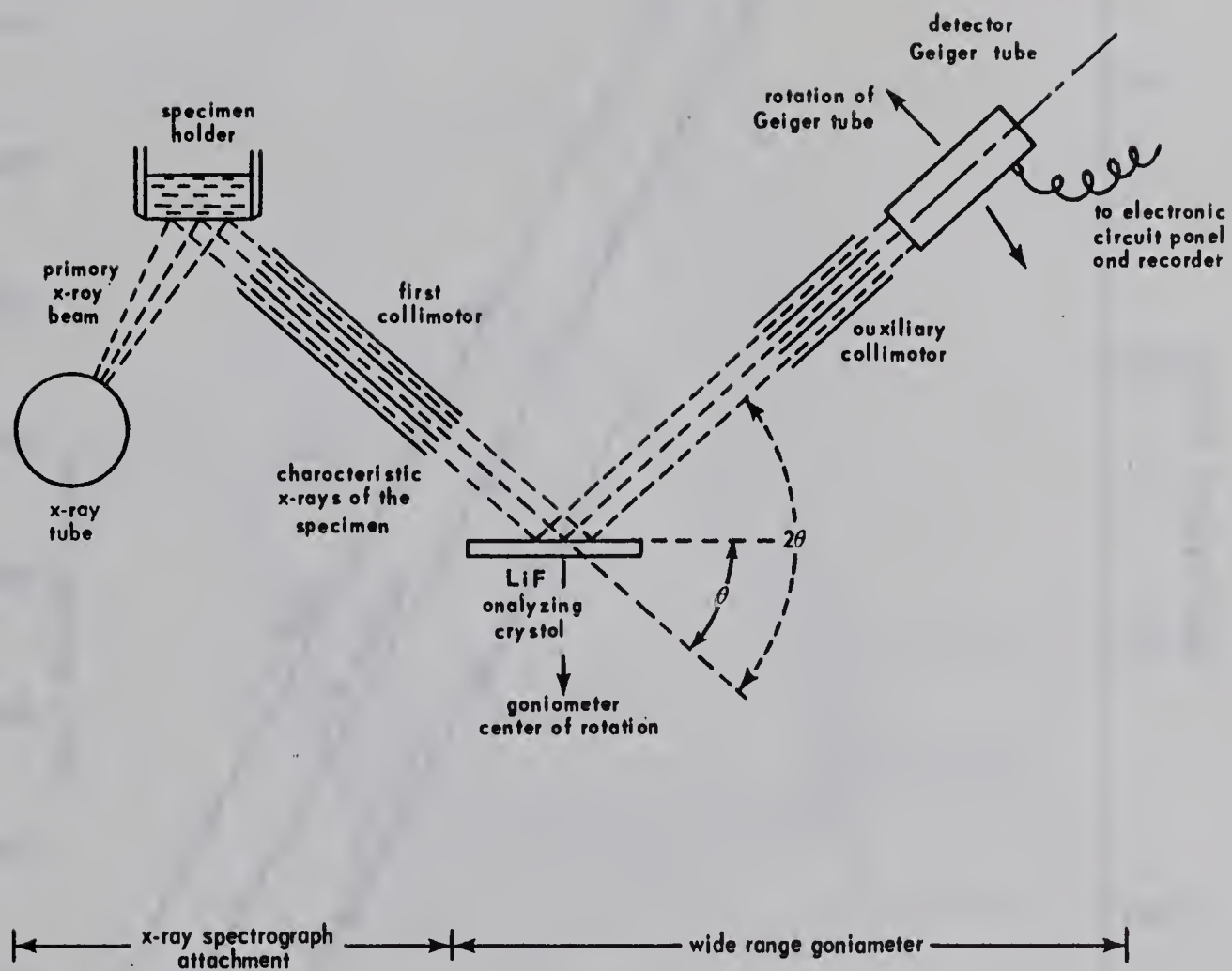


Fig. 50. Spectrophotometric determination of the composition of adduct between VDEHPA and beta-Collidine.



Diagrammatic Arrangement of the Plane-Crystal
Philips X-ray Fluorescence Spectrometer

Fig.51.

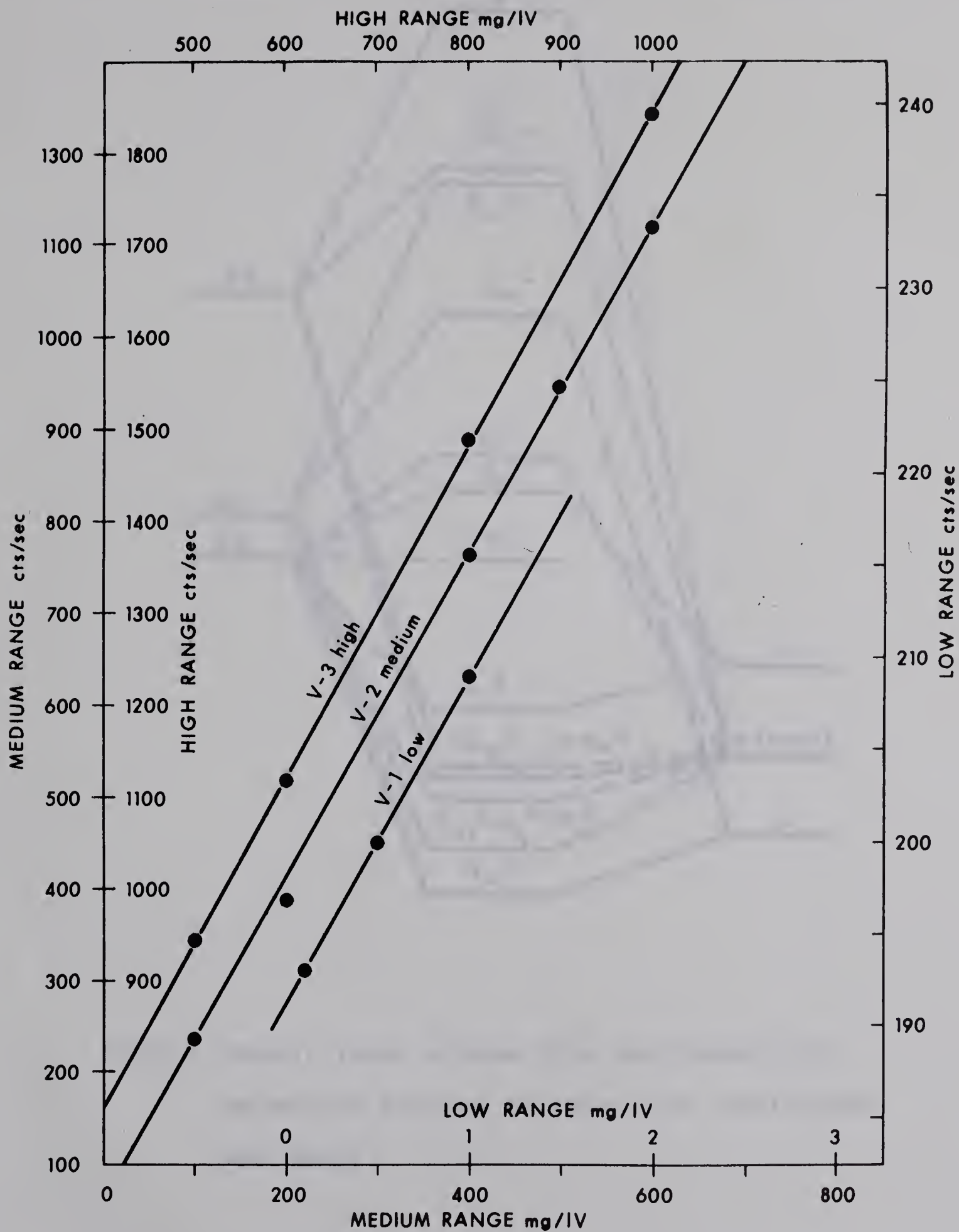


Fig.52. A representative standard curve for the estimation of V by X-Ray fluorescence spectrometer.

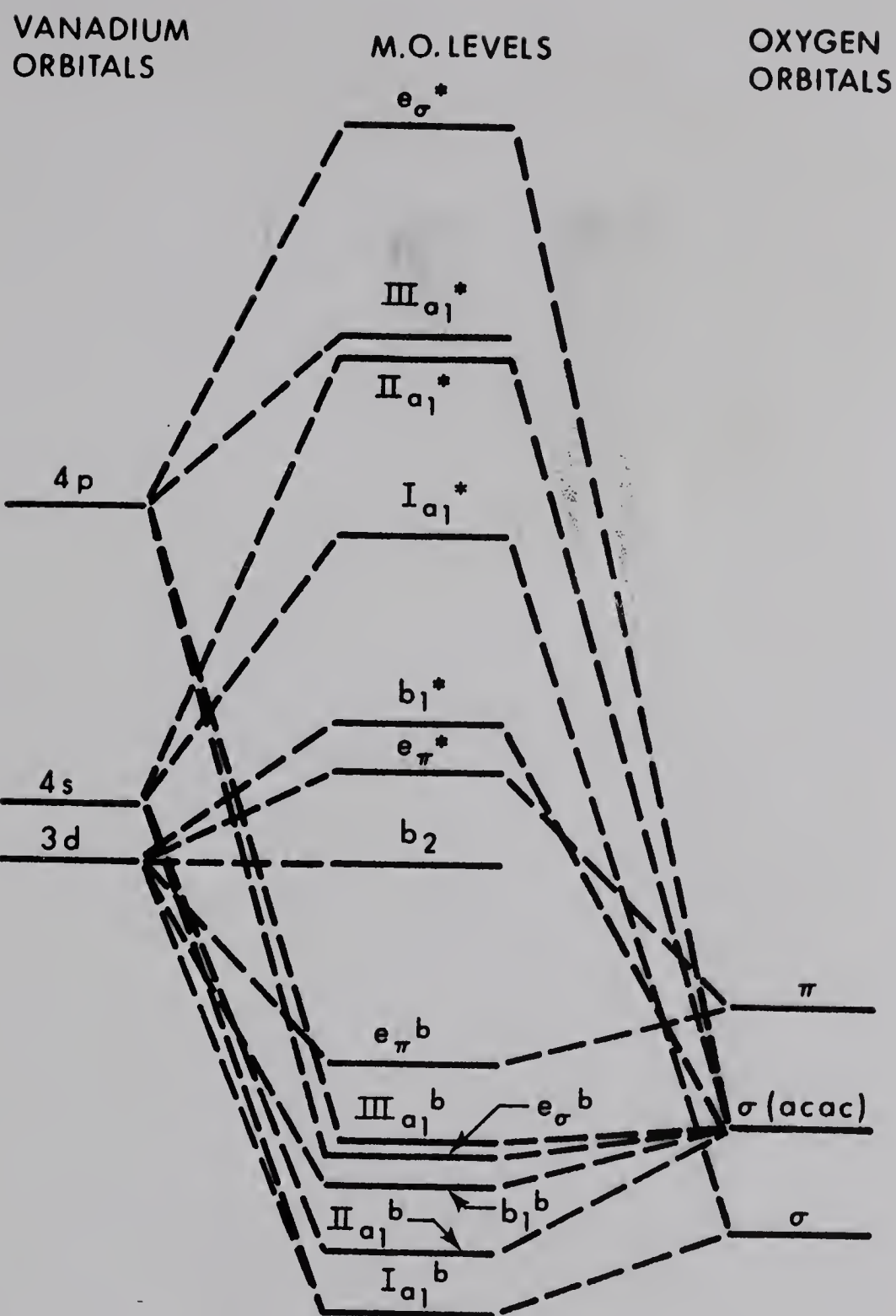


Fig.53. Energy level scheme from semi-empirical molecular orbital calculations (Ballhausen and Gray).

B29867